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**Microbiology.** — *Some remarks on the reduction intensity of living cells.*

By A. J. KLUYVER and J. C. HOOGERHEIDE.

(Communicated at the meeting of February 29, 1936).

Ever since micro-organisms have been studied attention has been drawn to the reduction phenomena which are caused by their activities. Already in 1844 HELMHOLTZ<sup>1)</sup> observed that litmus was decolorized in a medium containing putrifying proteins and he clearly proved the reduction character of this change by showing that on shaking the liquid with air the original colour was again obtained.

The classical researches of EHRLICH<sup>2)</sup> on the avidity for oxygen of the various organs of the animal body mark a milestone in the development of our knowledge of biological reductions, because they gave a convincing demonstration of the usefulness of certain dyes for the differentiation of the reduction intensities of different cells.

From this time on numerous observations regarding the behaviour of living cells towards various dyes have been recorded, but a just evaluation of the results obtained has been only made possible by the fundamental studies of CLARK and collaborators<sup>3)</sup> on the principles underlying the oxidation and reduction of a great number of so-called redox indicators.

Moreover, building on some preliminary observations made by POTTER<sup>4)</sup> and by GILLESPIE<sup>5)</sup>, the last mentioned investigators have emphasized that a more exact quantitative determination of the reduction intensity of living cells could probably be based on the direct electrometric measurement of oxidation-reduction potentials which manifest themselves in suspensions and in culture media of these cells.

The work of CLARK et al. has greatly stimulated the interest in this field and in later years very numerous publications have appeared which deal with oxidation reduction potentials in their relation with biological systems; we may refer here to the monographs of MICHAELIS, WURMSER and HEWITT in which a survey of this work has been given<sup>6)</sup>.

A closer inspection of the literature in question shows, however, that

<sup>1)</sup> H. HELMHOLTZ, Journ. f. prakt. Chem. **31**, 429 (1844).

<sup>2)</sup> P. EHRLICH, Das Sauerstoff-Bedürfnis des Organismus. Eine farben-analytische Studie. Berlin (1885).

<sup>3)</sup> W. MANSFIELD CLARK et al., Studies on Oxidation-Reduction I—X, U. S. Public Health Service, Hyg. Lab. Bull. **151** (1928) and subsequent papers.

<sup>4)</sup> M. C. POTTER, Proc. Royal Soc. Ser. B., **84**, 260 (1911).

<sup>5)</sup> L. J. GILLESPIE, Soil Science, **9**, 199 (1920).

<sup>6)</sup> L. MICHAELIS, Oxydations-Reductions-Potentiale. 2te Aufl., Berlin (1933); R. WURMSER, Oxydations et réductions. Paris (1930); R. WURMSER, L'électroactivité dans la chimie des cellules. Paris (1935); L. F. HEWITT, Oxidation-reduction potentials in bacteriology and biochemistry. 3rd Ed., London (1935).



by far the greater part of these publications bears a more or less empirical character. They reveal that in culture media containing growing micro-organisms remarkable changes in oxidation-reduction potentials occur. Yet, as a rule, the authors fail to connect the results of their observations with any characteristic property of the cells under consideration. If we may ascribe to the potentials observed any significance for the evaluation of the reduction intensity of cells then the conclusion can only be that this property is liable to considerable variations under the influence of several badly known factors.

There is, however, a restricted number of investigations in which a direct relation between the potentials observed and the chemical nature of the metabolism of the cells is established beyond doubt. We will cite here only the papers of QUASTEL and WHETHAM<sup>1)</sup>, LEHMANN<sup>2)</sup>, BORSOOK and SCHOTT<sup>3)</sup>, WURMSER and MAYER<sup>4)</sup> and of SZENT-GYÖRGYI<sup>5)</sup>.

Since recent development of our knowledge of biochemical conversions has thrown a clear light on the preponderant rôle of oxidation-reductions in these processes, it seems indeed probable that the metabolic processes will play an essential part in the establishment of the potential difference between a noble metal electrode and the medium of the cells.

A more systematic study of the relation between the metabolism of various cells and redox potentials occurring in their media appeared, therefore, to be of real interest.

It is obvious that for studies of this nature it will offer many advantages if the activities of the cells are examined in a medium of a simple, well-defined composition. Under these conditions the nature of the prevalent metabolic processes can be established with certainty and only then a clear answer to the question whether these processes determine the value of the redox potentials in the media can be expected.

Experiments performed in this laboratory by ELEMA<sup>6)</sup> have shown definitely, that indeed in suspensions of denitrifying bacteria in a medium containing only nitrate, phosphate and a simple organic compound like ethyl alcohol reproducible potentials can be determined and that the value of these potentials is clearly dependent on the nature of the katabolic processes of the bacteria.

A second proof for the existence of such a relation was given by the present authors<sup>7)</sup> in an investigation of the redox potentials occurring in

1) J. H. QUASTEL and M. D. WHETHAM, *Biochem. J.*, **18**, 519 (1924).

2) J. LEHMANN, *Skand. Arch. f. Physiol.*, **46**, 339 (1925).

3) H. BORSOOK and H. F. SCHOTT, *Journ. Biol. Chem.*, **92**, 535 (1931).

4) R. WURMSER et N. MAYER, *Compt. rend. Acad. Sc.*, **195**, 81 (1932).

5) A. SZENT-GYÖRGYI, *Zeitschr. f. physiol. Chem.*, **217**, 51 (1933).

6) B. ELEMA, De bepaling van de oxydatie-reductiepotentiaal in bacteriëncultures en hare beteekenis voor de stofwisseling. Delft (1932); B. ELEMA, A. J. KLUYVER and J. W. VAN DALFSEN, *Biochem. Zeitschr.*, **270**, 317 (1934).

7) A. J. KLUYVER und J. C. HOOGERHEIDE, *Biochem. Zeitschr.*, **272**, 197 (1934); J. C. HOOGERHEIDE, *Bijdrage tot de kennis van de reactie van Pasteur*. Delft (1935).

suspensions of yeast cells under conditions of full metabolic activity. Here it was found that the values of the potentials observed were determined by the relative intensities of the two katabolic processes of the yeast, i.e., fermentation and respiration.

The question now arises in how far the potentials observed in these experiments may be considered as characteristic for the reduction intensity of the cells under the conditions of the experiment, i.e., for the ability of the cells to reduce or not to reduce under these conditions reversible redox systems with normal potentials situated respectively either higher or lower than the potentials measured.

Although in our preceding publications no definite opinion has been expressed as to this point, yet it is easily understood that such an assumption has been tacitly made. At first we too have been inclined to subscribe to this view. The results of a recent investigation by FROMAGEOT and DESNUELLE<sup>1)</sup> — more particularly the demonstration of the ability of fermenting yeast to reduce nil blue — have, however, at once thrown considerable doubt as to the validity of the said conclusion. Therefore we have decided to examine this point in more detail. The results of our researches are briefly discussed below.

It seems unquestionable that, if a noble metal electrode on immersion in an aqueous medium, shows a constant and reproducible potential difference against this medium, the latter will contain a reversible redox system in a state of partial reduction<sup>2)</sup>. Now in the majority of the experiments with the denitrifying bacteria and with the yeast cells referred to above no such redox indicator had been added, the only constituents of the media employed being either substances like ethyl alcohol, nitrates and phosphates (denitrifying bacteria) or sugar and phosphates (yeast cells). If, therefore, in these media too characteristic potentials manifest themselves, it must be concluded that in these cases reversible redox systems have been excreted by the cells in the suspension. This conclusion has indeed been drawn by ELEMA (l.c.) who at the same time introduced the term "bio-indicator" to denote the systems in question. Experimental proof for the correctness of this assumption was brought in the paper by ELEMA, KLUYVER and VAN DALFSEN (l.c.) and later also by YUDKIN<sup>3)</sup>.

When on the other hand one observes that the potentials measured at the electrode vary with the metabolic activities of the cells present in the

<sup>1)</sup> CL. FROMAGEOT und P. DESNUELLE, *Biochem. Zeitschr.*, **279**, 34 (1935).

<sup>2)</sup> It is a fact of common experience that a given redox system only determines a reproducible potential at a noble metal electrode as long as the equilibrium between the oxidized and reduced component of the system is not too much shifted to one side. In practice, working with low concentrations of the redox system, at least about 5% of the system should be present either in its oxidized or in its reduced state. This requirement limits the potential determining activity of a given redox system to a range of about 30 millivolt above or below its normal potential.

<sup>3)</sup> J. YUDKIN, *Biochem. Journ.*, **29**, 1130 (1935).



medium, one cannot escape the conclusion that the electro-active system responsible for the potential observed enters the cells in question and that the state of equilibrium between the oxidized and the reduced component of the system will be changed on the surface of the cell catalysts.

These considerations imply that an electrometrically determined potential will only then be an expression for the reduction intensity of the cells under the conditions of the experiments, in so far as the medium contains a redox system answering the two requirements formulated above, namely, that the system is present in a partially reduced state and is capable of entering the cells.

Now the results obtained in the yeast experiments, showed that indeed yeast cells do excrete such redox systems, the normal potentials, of which obviously cover a wide range. For at a  $p_H=5.4$ , dependent on the degree to which either respiration or fermentation prevailed, values of  $E_h$  had been observed varying between + 300 and + 60 millivolt.

Nevertheless there seems to be no reasonable ground why living cells should excrete such systems over the whole range covered by the variations in reduction intensity of these cells. This consideration has induced us to repeat our experiments on the redox potentials observable in the media of yeast cells under conditions of full metabolic activity but this time after addition of small quantities of suitable redox indicators (dyes of known normal potentials) to the medium.

In the first place attention has been given to the redox potentials occurring in yeast suspensions in phosphate-buffer ( $p_H=5.4$ ) containing 5 % glucose under completely anaerobic conditions. It was ascertained beforehand that the addition of the various redox systems in the very low concentration employed did not alter the rate of fermentation to any appreciable extent.

It seemed desirable to test the influence of a large series of redox indicators, the normal potentials of which at  $p_H=5.4$  varied between + 150 and -236 millivolt.

The results of these experiments are collected in the following table to which may be remarked that the final  $p_H$  in the media proved to be 5.2.

At first sight one is struck by the diversity of the potentials measured in the various experiments. A closer inspection shows, however, that in the majority of cases a potential is reached which lies in the region between +40 and +90 millivolt, that is the same region which was found in our former experiments in the absence of added indicators. It is especially noteworthy that this applies for all cases in which indicators with high normal potentials (from 80 millivolt upwards) or with low normal potentials (from -74 millivolt downwards) are used.

This indicates that these dyes in the potential region as determined by the fermentation occur in the nearly completely oxidized or in the nearly completely reduced state respectively and for this reason are unable to control the electrode.

Redox indicator	$E'_0$ in Millivolt at $p_H = 5.4$	$E_h$ in Millivolt (after 20 hours)
Prune . . . . .	150	90
Thionine . . . . .	118	78
Gallocyanine . . . . .	116	42
Toluidine blue . . . . .	86	67
Methylene blue . . . . .	80	49
Pyocyanine . . . . .	56	— 6
Janus green . . . . .	(46)—144	—12
Indigo tetrasulphonate . . . . .	36	118
Indigo trisulphonate . . . . .	6	83
Chlororaphine . . . . .	— 18	—40
Nil blue . . . . .	— 34	—43
Gallophenine . . . . .	— 36	67
Indigo disulphonate . . . . .	— 36	73
Brilliant alizarine blue . . . . .	— 74	88
Anthrachinone 1—5 disulphonate . . . . .	— 84	90
Phenosafranine . . . . .	—159	—
Rosinduline . . . . .	—185	42
Neutral red . . . . .	—236	50

Obviously the lowest values observed, viz. those in the presence of chlororaphine and of nil blue, must be considered as the limit of the reduction intensity of the yeast cells under the condition of alcoholic fermentation. For if indeed lower potentials than —43 millivolt (at  $p_H = 5.2$ ) could be brought about by the yeast there is no reasonable ground why these should not be indicated by the electrode since both indicators (especially nil blue) are still able to control it at markedly lower potentials (Cf. note 2, page 243).

If we accept this view part of the remaining abnormal potentials can be readily explained. For at this particular reduction level indicators like pyocyanine, Janus green (first reduction step) and indigo tetrasulphonate will occur in a too highly reduced state to be still able of control of the electrode.

Only the behaviour of indigo trisulphonate, gallophenine and indigo disulphonate seems to contradict the statement made. The explanation for this apparent deviation was, however, soon found in the experimental



proof that these indicators — in contrast to chlororaphine and nil blue — do not enter the cells; they do not belong to the group of vital stains as is corroborated by the findings of other investigators.

The same value for  $E_h$  of about  $-40$  millivolt (at  $p_H = 5.2$ ) has since approximately been found back in numerous experiments, in which different yeast species and also other sugars than glucose have been applied. The investigation of *Pseudomonas Lindneri*, a bacterium which brings about a nearly pure alcoholic fermentation of glucose, led to the same result.

All this seems to warrant the conclusion that the said value, corresponding to a  $r_{H_2} = 9.0$ , is characteristic for the reduction intensity of all cells under the conditions of alcoholic fermentation.

Since the foregoing experiments had shown convincingly that in determining reduction intensities it is inadmissible to rely in all instances on the natural redox systems excreted by the cells, we have also repeated our former experiments regarding the potentials occurring in suspensions of yeast cells in contact with oxygen, i.e. under conditions in which besides fermentation also respiration proceeds.

It was found that in these cases addition of suitable redox indicators did not affect the potential levels observed in the absence of these indicators to an appreciable extent. Apparently in this, much higher situated, potential region the natural redox systems excreted by the yeast cells suffice to control the electrode. The potentials observed may, therefore, be considered to be characteristic for the reduction intensities of the yeast cells under the special metabolic conditions of each experiment.

It seemed of interest to make similar observations in suspensions of cells which are characterized by another, yet also simple, way of anaerobic sugar breakdown.

As such we have chosen homofermentative lactic acid bacteria, of which numerous species belonging to various morphological groups (genera: *Thermobacterium*, *Streptobacterium* and *Streptococcus*) have been examined. All these bacteria convert glucose almost quantitatively into lactic acid.

The results will only very briefly be reported here.

In phosphate buffer with 2 % glucose but without addition of redox systems the potentials sank only gradually and the levels attained proved to be not well reproducible. This seemed to indicate that in this case too for the determination of the reduction intensity of the cells it was not permitted to rely on the natural redox systems excreted by the bacteria. Therefore the experiments were repeated but now after addition of a suitable mixture of redox indicators with decreasing normal potentials. Under these conditions a very definite reduction level was quickly attained.

In presence of a mixture of nil blue, Janus green, phenosafranine and neutral red (in a concentration of 0.00025 % each) the potentials listed

in the following table were observed. Since owing to the production of a rather considerable quantity of lactic acid, it proved impossible to maintain fully the initial  $p_H$ , attention should be given more especially to the recalculation of the reduction intensity in terms of  $r_{H_2}$  (last column).

Bacterial species	$E_h$ in millivolt at the end of the experiment	Final $p_H$	$r_{H_2}$
<i>Thermobacterium Delbrücki</i> a . . . . .	-163	5.5	5.6
"      "      b . . . . .	-156	5.5	5.8
<i>Thermobacterium bulgaricum</i> . . . . .			
<i>Streptobacterium plantarum</i> a . . . . .	-190	5.9	5.5
<i>Streptobacterium casei</i> b . . . . .	-186	5.9	5.6
<i>Streptococcus lactis</i> a . . . . .	-168	5.4	5.2
"      "      b . . . . .	-208	6.0	5.4
<i>Streptococcus cremoris</i> a . . . . .	-192	5.8	5.2
<i>Streptococcus faecium</i> a . . . . .	-228	6.3	5.0
"      "      b . . . . .	-180	5.6	5.2
<i>Streptococcus bovis</i> a . . . . .	-189	5.6	4.9
"      "      b . . . . .	-222	6.3	5.2
<i>Streptococcus amylo lactis</i> a . . . . .	-151	5.0	5.0
"      "      b . . . . .	-95	4.1	5.0
<i>Streptococcus mastitidis</i> a . . . . .	-210	6.0	5.0
"      "      b . . . . .	-214	6.1	5.1
<i>Streptococcus liquefaciens</i> . . . . .	-201	6.1	5.5
<i>Streptococcus agilis</i> . . . . .	-173	5.8	5.8

The figures obtained do not leave any doubt that the reduction intensity of all cells under the conditions of active lactic acid fermentation can be represented by a value of  $r_{H_2}$  between 5.0 and 6.0. These values contrast well with the values of  $r_{H_2}$  between 8.4 and 9.0 as found for cells under the conditions of alcoholic fermentation.

The result that all lactic acid bacteria examined, independent of their specific properties, lead to practically one and the same reduction level may be deemed to be rather remarkable. For in bacteriological literature several instances can be found which seem to contradict this statement.



Thus SHERMAN and ALBUS<sup>1)</sup>, AVERY<sup>2)</sup>, RUDOLPH<sup>3)</sup>, a.o. have applied the different behaviour of various *Streptococcus* species in milk containing either litmus, or methylene blue, or neutral red for the differentiation of humane and bovine streptococci from those of other groups. CLARK<sup>4)</sup> in his fundamental paper on methylene blue refers to these investigations and states explicitly that the differences observed should now be expressed in numerical values for reduction intensity of the various species.

In order to elucidate this contradiction we have made a special inquiry into this matter. Although we must refrain from giving any details here, we may state that the results obtained show clearly that in no instances are the differences observed visually due to differences in reduction intensity of the cells in question.

From the experiments reported and the considerations given we wish to conclude:

1. The reduction intensity of the living cell is only in a restricted sense a specific property of the cell, in so far as this intensity is at any moment determined by the nature of the metabolic processes occurring in the cell.

2. The oxidation-reduction potentials in media of living cells under well-defined metabolic conditions may be considered characteristic for the reduction intensity of the cells under these conditions, provided that the medium contains a partially reduced redox system, capable of penetrating the cells.

3. Although, as a rule, living cells excrete into their medium several reversible redox systems which together often are able to control an electrode over a wide region of potentials, yet it is not permitted to accept that in all cases such systems will cover the whole range of the reduction intensity of the cells. Therefore, a redox potential measured electrometrically in the medium is only then characteristic for the reduction intensity of the cells under the conditions of the experiment, if the addition of a small quantity of a redox system answering the requirements formulated under 2 does not alter the potential.

A more extensive publication, in which full particulars regarding the experiments will be given, will appear elsewhere.

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<sup>1)</sup> J. M. SHERMAN and W. R. ALBUS, Journ. of Bact., **3**, 168 (1918).

<sup>2)</sup> R. C. AVERY, Bact. Abstracts, **6**, 31 (1922).

<sup>3)</sup> J. RUDOLF, Centralbl. f. Bakt. I Abt., **100**, 147 (1926).

<sup>4)</sup> W. MANSFIELD CLARK, Studies on Oxidation-Reduction, VIII, Public Health Reports, Washington **40**, 1131 (1925).

**Embryology.** — *Embryonic "induction" by chemical substances.* By  
M. W. WOERDEMAN.

(Communicated at the meeting of February 29, 1936).

SPEMANN and his pupils showed that during embryonic development an interaction exists between special cell groups in the embryo, which has been named "inductive action".

It was conjectured that the roof of the archenteron influences the adjacent ectoderm of amphibian embryos, which causes this ectodermal region to respond with the formation of a neural plate. If now experimentally part of the roof of the archenteron is grafted under indifferent ectoderm, the latter reacts by differentiating into a neural plate (or part of it) above the graft. It is surmised that by "inductive action", proceeding from the implant (which is called "inductor"), out of the indifferent ectoderm a neural plate has originated.

On account of this experiment and many others it is practically certain that also in normal development the neural plate is formed by inductive action emanating from the roof of the archenteron.

Experimental researches proved that not only the roof of the archenteron has an "inductive capacity" but that other cell groups possess this capacity as well. It is besides not only the neural plate which originates by an inductive action but other organs also are induced from indifferent material by neighbouring inductors (e.g. the lens by the eyecup).

During the latter years many researches have been devoted to this mysterious inductive action.

It can, of course, be of a highly varying nature, but very soon the conception got the upper hand that it is produced by chemical substances.

Particularly the observation that inductors killed by heating, freezing, drying and treatment with alcohol appeared not to have lost their inductive capacity supported this supposition <sup>1, 2</sup>). By treating inductors with various reagents or extracting them with solvents and then examining their inductive capacity, it was tried to determine the properties of the "inductive substance". Or inductors were extracted and it was tried to separate special fractions from the extract, which then in some vehicle or other (e.g. agar-agar or gelatin) were grafted under indifferent ectoderm in order to find whether they produced an inductive action.

F. G. FISCHER and E. WEHMEIER, among others, worked in this way and in a "Nachtrag" in the same number of "Die Naturwissenschaften".

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<sup>1</sup>) H. BAUTZMANN, J. HOLTFRETER, H. SPEMANN u. O. MANGOLD, *Naturwissenschaften* 20<sup>51</sup>, Dezember (1932).

<sup>2</sup>) J. HOLTFRETER, *Arch. f. Entw.mech.* 128<sup>3</sup>, 584 (1933).



where they communicated their results <sup>3)</sup>, they arrived at the conclusion, not further explained by arguments, that glycogen would be the inductive substance. Meanwhile I had already pointed to the typical metabolic processes in the inductors, which are accompanied by the disappearance of glycogen <sup>4)</sup>, and on account of this observation I had also occupied myself with the investigation of the inductive capacity of glycogen, which however led to negative results <sup>5)</sup>.

HOLTFRETER <sup>6)</sup> and J. NEEDHAM, C. H. WADDINGTON and D. M. NEEDHAM <sup>7)</sup> also considered glycogen inactive and it is practically certain that FISCHER and WEHMEIER worked with glycogen containing traces of an inductive substance <sup>8)</sup>. FISCHER and WEHMEIER <sup>3)</sup> and also HOLTFRETER <sup>2)</sup> had observed that parts of amphibian embryos, which in living state did not produce an inductive action, began to do this after being killed by treatment with certain reagents. On this basis FISCHER and WEHMEIER built their hypothesis that in certain living cells by the side of inductive substances also an "inhibitor" substance should occur. By extraction of the inhibitor, the part of the egg killed by the extracting solvent (ether) would become an inductor.

Towards the end of 1933 some important communications were published, from which it appeared that the inductive substance occurs not only in some embryonic cell groups but also in many organs of adult invertebrate and vertebrate animals, but is not observed in vegetable substances, while further from newt larvae and from the organs of adult newts a petrol-ether extract could be prepared, which contains the active substance <sup>9, 10)</sup>.

HAMPE demonstrated in my laboratory the inductive capacity of pathological tissues (rat's mamma-carcinoma, human mamma-carcinoma, PEYTON ROUS fowl sarcoma) and mammalian muscular tissue <sup>4c&d)</sup>.

Since various organs and tissues, easily obtainable in large quantities, contain inductive substance, it was possible to isolate this substance in a sufficient amount.

Especially in the laboratories of J. NEEDHAM (Cambridge, Eng.) and

<sup>3)</sup> H. SPEMANN, F. G. FISCHER u. E. WEHMEIER, *Naturwissenschaften* **21**<sup>27</sup>, Juli (1933).

<sup>4)</sup> M. W. WOERDEMAN, a) *Proc. Royal Acad. Amsterdam*, **36**, 189, Febr. (1933); b) **36**, 423, April (1933); c) **36**, 477, May (1933); d) *Ned. Tijdschr. v. Geneesk.* **77**, 31, 3621 (1933).

<sup>5)</sup> M. W. WOERDEMAN, *Proc. Royal Acad. Amsterdam*, **36**, 842, Sept. (1933).

<sup>6)</sup> J. HOLTFRETER, *Naturwissenschaften*, **21**<sup>43</sup>, October (1933).

<sup>7)</sup> J. NEEDHAM, C. H. WADDINGTON and D. M. NEEDHAM, *Proc. Royal Soc. London, B.* **114**, 393 (1934).

<sup>8)</sup> C. H. WADDINGTON, J. NEEDHAM, W. W. NOWINSKI, D. M. NEEDHAM and R. LEMBERG, *Nature*, **134**, 103 (1934).

<sup>9)</sup> C. H. WADDINGTON, JOSEPH and DOROTHY M. NEEDHAM, *Nature*, **132**, 239, Aug. (1933).

<sup>10)</sup> C. H. WADDINGTON, JOSEPH and DOROTHY M. NEEDHAM, *Naturwissenschaften* **21**<sup>43</sup>, Okt. (1933).

F. G. FISCHER (Freiburg in Br.) this work was taken in hand, while meantime by experimental-embryological researches in numerous laboratories the peculiarities of the induction by chemical substances were studied more closely. The conception of FISCHER and WEHMEIER that also (an) inhibitor substance(s) would exist was not supported by this continued research. HOLTFRETER<sup>6)</sup>, J. NEEDHAM, C. H. WADDINGTON and D. M. NEEDHAM<sup>7)</sup> reject the hypothesis of the presence of inhibitor substances, and in her elaborate publication of 1934 ELSE WEHMEIER<sup>11)</sup> does not further discuss the presence of inhibitor substance(s).

As to the chemical researches: thus far they have not yet led to corresponding results.

NEEDHAM and his collaborators suppose that the inductive substance is soluble in ether and petrol-ether<sup>9)</sup> and, on a continued purification of ether extracts from organs with inductive action, came to the conclusion that the inductive substance is a sterol-like body<sup>7, 8)</sup>. They could with two synthetically prepared phenanthrene compounds obtain induction of neural plates.

FISCHER, WEHMEIER and JÜHLING<sup>12)</sup>, on the other hand, are inclined to think that induction of neural plates may be obtained by muscular adenylic acid and thymonucleic acid.

Now it is not impossible that more than one inductive substance exists and in HOLTFRETER's publications<sup>13)</sup> it is seen that this author takes the existence of several inductive substances into consideration.

NEEDHAM c.s.<sup>14)</sup>, however, assume that the muscular adenylic acid and thymonucleic acid of FISCHER c.s., prepared from animal organs, do not produce an inductive action themselves but that their action is due to inductive substances which they contain as impurities. The same should be the case with cephalin, prepared from brains by BARTH<sup>15)</sup>, to which BARTH also ascribes inductive action. NEEDHAM c.s. still seek the inductive substance(s) among the sterol-like compounds, point to the connection with oestrogenic and carcinogenic substances and have tried the inductive action of many products from this group of substances. WADDINGTON and D. M. NEEDHAM<sup>16)</sup> then made the important observation that a substance, whose strongly carcinogenic properties are known, viz. the 1:2:5:6-dibenzanthracene, appeared also to be able to induce a neural plate in one case.

Evidently it is possible to obtain neural induction with several syntheti-

<sup>11)</sup> ELSE WEHMEIER, Arch. f. Entw.mech. **132**<sup>2—3</sup>, 384 (1934).

<sup>12)</sup> F. G. FISCHER, E. WEHMEIER und L. JÜHLING, Nachr. Ges. Wiss. Göttingen, Abt. Biol., 394, Nov. (1933).

<sup>13)</sup> J. HOLTFRETER, Arch. f. Entw.mech. **132**<sup>2—3</sup>, 306 (1934).

<sup>14)</sup> C. H. WADDINGTON, J. NEEDHAM, W. NOWINSKI and R. LEMBERG, Proc. Royal Soc. London, B. 804, Vol. **117**, 289 (1935).

<sup>15)</sup> L. G. BARTH, Biol. Bull. **67**, 244 (1934).

<sup>16)</sup> C. H. WADDINGTON and D. M. NEEDHAM, Proc. Royal Soc. London, B. 804, Vol. **117**, 310 (1935).



cally prepared substances. It is another question, however, which substance plays a role in normal embryonic induction. In a recent article <sup>17)</sup> now FISCHER and his collaborators communicated that the preparations described by NEEDHAM c.s. as active could be made inactive by freeing them from traces of acid. Further they obtained induction with synthetically prepared oleic acid. They think that several fatty acids and nucleic acids have an inductive action and arrive at the final conclusion that the inductive action may be an acid-stimulation.

Meanwhile also in our laboratory many experiments had been made in order to get a better insight into the problem of induction. They were carried out partly by HAMPE, partly by myself. HAMPE examined the inductive capacity of numerous substances, such as press juice from muscular tissue and from tumours; ether extracts from these tissues and the remaining residue; glycogen derived from muscular tissue, before and after its being defatted and petrol-ether extraction; boiled and dried muscular tissue; tripalmitin, tributyrin, tristearin and triolein, beef fat; monobutyryn and glycerin, and various substances which might receive consideration as vehicles for the chemicals which are often very difficult to graft into a host gastrula.

In connection with my observations on the loss of glycogen in inductors, I myself examined the inductive action of glycogen and its decomposition products, products of carbohydrate fermentation, lactic acid, butyric acid, and of fermentative and oxidation processes, which I caused to take place under indifferent ectoderm of axolotl-blastulae and gastrulae.

At the same time, on account of the observations made in our laboratory with tumour-tissue, which were confirmed by WEHMEIER <sup>11)</sup>, I examined the action of a carcinogenic substance, 1 : 2 : 5 : 6-dibenzanthracene, kindly placed at my disposal by Prof. Dr. H. T. DEELMAN. We did not publish the results of our investigation: in the first place because meanwhile the results of similar or completely equal experiments had been elaborately communicated by others <sup>6, 7, 8, 11, 13, 14, 16)</sup>, but secondly because I began to doubt whether they had attached the correct meaning to their results.

The technique of the investigation into the inductive capacity of a special material is usually the following. The material is grafted into the blastocoel of an amphibian blastula. Mostly after gastrulation it has got its position somewhere under the ectoderm. Where this will be, cannot be said beforehand. It has now become apparent that it is by no means insignificant where the "graft" happens to be situated.

Before the beginning of the research on chemical factors in the induction, observations among others by RAVEN <sup>18)</sup>, made in our laboratory, had drawn our attention to this phenomenon.

<sup>17)</sup> F. G. FISCHER, E. WEHMEIER, H. LEHMANN, L. JÜHLING und K. HULTZSCH, *Ber. d. dtsh. chem. Gesellsch. Jhg.* **68**, H. 6, 1196 (1935).

<sup>18)</sup> CHR. P. RAVEN, a) *Proc. Royal Acad. Amsterdam*, **34**, 554 (1931); b) *Ned. Tijdschr. v. Geneesk.* **75**, II, 35 (1931); c) *Arch. f. Entw.mech.* **130**<sup>3-4</sup> (1933).

RAVEN examined the inductive capacity of small pieces of neural crest. If such an inductor came to be situated in the neighbourhood of the neural plate of the host (Triton), it induced a small neural plate; if it took its position in the region of the so-called balancer (organ of RUSCONI), supernumerary balancers were formed. The effect of the inductive action consequently appeared to depend on the place where it is produced. Since also neural crest of *Rana* (the larvae of which possess no balancers), introduced into Triton, induced extra balancers, this result must be an indication that the inductive action in RAVEN's experiments is not specific and that the nature of the induced organ is chiefly dependent on factors working in the host.

However, cases are also known of inductors which, irrespective of the place in the host where they come to be situated, always induce the same organs and where consequently the effect of the inductive action is determined by the nature of the inductor (SPEMANN<sup>19</sup>).

The researches by RAVEN a.o. led me, in imitation of SPEMANN<sup>20</sup>), WEISS<sup>21</sup>), and GURWITSCH<sup>22</sup>), to assume the existence of "organ fields" in the embryo<sup>23</sup>). It should be imagined that in the embryo regions exist where the physical and chemical factors are such as to make it possible that a special organ is formed there ("embryonic field"). The organ originates in the centre of the field, where the "field action" is most intensive, but remains surrounded for some time by more or less extensive parts of the field which have not been used for the organ formation and where the field action is not very intensive.

If an inductor comes to be situated under the ectoderm of the host, the effect is in the first place dependent on the field within the domain of which the inductor comes to lie (in "neural plate field" the inductors used by RAVEN produced induction of neural plates and in "balancer field" formation of supernumerary balancers). But in the second place the result of the experiment will depend on the inductor, namely, on the power of its own embryonic field. If this is more powerful than the field action in the field within which the inductor is situated, the nature of the induced organ will be dependent on the inductor.

The observations on induction by chemical substances now have led me to conclude that the chemical substances and dead grafts, to which inductive action has been ascribed, merely influence existing embryonic fields, but that they do not produce a field action themselves. Their effect

<sup>19</sup>) H. SPEMANN, Arch. f. Entw.mech. **123**, 389 (1931).

<sup>20</sup>) H. SPEMANN, Arch. f. Entw.mech. **48**, 533 (1921).

<sup>21</sup>) P. WEISS, a) Naturwissenschaften **11**, 669 (1923); b) Arch. f. Entw.mech. **104**, 359 (1925); c) Arch. f. Entw.mech. **107**, 1 (1926).

<sup>22</sup>) A. GURWITSCH, a) Arch. f. Entw.mech. **51**, 383 (1922); b) Arch. f. Entw.mech. **112**, 433 (1927).

<sup>23</sup>) M. W. WOERDEMAN, Ann. Soc. Sciences méd. et natur. Bruxelles, 1932<sup>3-4</sup> et 5-6.

is dependent on their position in the host and neither in my own experiments nor in the data from the literature do I see arguments in favour of another conception.

For this reason we have to ask whether we can indeed speak of "inductive substances". Several of the substances examined, if they are not situated near an active organ field (e.g. neural plate field), merely show a stimulating effect on the cells in the immediate surroundings of the graft. Cell multiplication, changes in cell form, etc. are seen but the formation of a typical organ or part of an organ is out of the question. If, however, a similar implant happens to lie near a neural plate, a small neural plate is formed. Evidently the dead grafts can activate the cells in their vicinity and the activity of the embryonic fields of the host. I would, therefore, regard the dead grafts and chemical substances as "activators" for the embryonic cells. They do not produce an inductive action; that is done by the living host into which they have been introduced.

Also in those cases where later by microscopic examination the induced formation appears to lie rather far away from the corresponding organ of the host (e.g. eye lens in the cardiac region), the above explanation need not be incorrect. Some organ fields are very extensive (in some amphibians belly ectoderm can form an eye lens, if it is transplanted above the eye cup) and, besides, the induced organ and the organ of the host at the moment of their formation may have been situated closely together and only later came to lie farther apart.

As an objection to my explanation of the action of the so-called chemical "inductive substances" might be adduced the results of some experiments by HOLTFRETER. He succeeded in cultivating isolated cell groups of amphibian blastulae in salt solution<sup>24</sup>). For a number of his researches, mentioned above, he made use of such cultivated cell groups. He studied the influence of killed inductors and of chemical products on these cultures and could, for example, perceive the formation of neural plates and neural tubes in cultivated ectodermal vesicles. We might be inclined to think that here the inductive action of the host cannot have played a role and that the formation of the neural plates has to be ascribed to the influence of the inductors.

However, particularly in these "inductions" we are struck by the peculiar character of the induced formations. No typical organs are formed, but formations which can hardly be recognized as parts of organs. Moreover, as a rule nothing points to a typical grouping of organ parts. Often a differentiation of the cells is observed without organ formation.

A typical "organization", therefore, is out of the question.

Moreover, HOLTFRETER's experiments with cultures of parts from

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<sup>24</sup>) J. HOLTFRETER, a) *Verh. dtsch. Zool. Ges.* 174 (1929); b) *Arch. f. Entw.mech.* 117, II, 421 (1929); c) *Arch. f. Entw.mech.* 124, 404 (1931); d) *Verh. dtsch. Zool. Ges.* 158 (1931).



blastulae showed that already in the blastula a certain differentiation exists and that such cultures even without the influence of inductors can ultimately form special tissues and even parts of organs. The cultures, consequently, are not completely indifferent and I suppose that the dead inductors have done nothing but increase field actions already present in the cultures, although only slightly active.

We are not compelled to assume that the chemical substances and dead "inductors" really "have brought something new into the cultivated cell material" (*inducere* = to bring into). Here also we can account for the phenomena observed by an activation of developmental tendencies which were already present.

In the literature several remarks are found from which it appears that the authors have doubted the "inductive action" of dead grafts and chemical substances.

NEEDHAM and WADDINGTON, for example, introduced the name "evocator". According to their conception, the dead graft or the chemical substance can produce a supernumerary "embryonic axis" but the "regional character" of the organs which will arise from this primordium is determined ("*individuation*") by "*individuation-fields*" active in the host (WADDINGTON and SCHMIDT<sup>25</sup>). I would go yet further and not even give the name "evocator" to the chemical substance or the dead implants. They activate the cell material, but the "evocation" of the supernumerary embryonic axis is the work of the host itself.

The graft, however, can determine the direction of the axis, as I was able to demonstrate by using long-stretched bits of an isolated muscle fibre as inductor. The axis of the induced neural plates was determined by the longitudinal axis of the muscle fibre.

But this is not surprising either, if it is borne in mind that the activating influence of the implant is only exerted on the cells with which it has direct contact. A long stretched graft will activate a long-stretched part of the embryonic neural plate field and the tendency of parts of the "field" to form a "totality" will be able to bring about that the induced neural plate comes to be situated in the direction of the activated field. In any case it is the embryonic field action, consequently the host, which "induces" the neural plate.

HOLTFRETER also elaborately discusses the difficult question what part in the process of induction is taken by the host and by the inductor. He is little decided in his statements; on the one hand he ascribes significance to the host but on the other hand considers the inductive substance of such importance that he is even inclined to assume different inductive substances for different organs<sup>26</sup>).

This problem also, which has been discussed several times in the literature, may be mentioned here.

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<sup>25</sup>) C. H. WADDINGTON and G. A. SCHMIDT, *Arch. f. Entw.mech.* 128, 522 (1933).

In my opinion it is an ascertained fact that with various chemical substances effects can be obtained which are called "induction". Whether this is due to a common property of all these substances, e.g. to a stimulation by acids <sup>17)</sup>, I leave aside. However, it is by no means surprising that several substances have been found showing the so-called "inductive capacity", now that we may assume that these substances should be considered merely as stimulating substances, as activators, and that the real induction itself is performed by the host. It is conceivable that embryonic fields can be activated also by other than chemical agents; mechanical and thermal stimulation even seems able to produce induction. <sup>14, 26, 27, 28)</sup>

We found that some substances were very powerful activators, whereas others only produced a feeble action. To the most powerful belonged petrol-ether extracts and press juice from tumours and muscular tissue. The carcinogenic substance 1:2:5:6-dibenzanthracene indeed caused strong proliferation of the ectoderm but I did not observe formation of neural tubes (in axolotl gastrulae). Consequently I can confirm the opinion of WADDINGTON and D. M. NEEDHAM <sup>16)</sup> that this substance is an activator; however, they once observed the formation of a neural tube in *DiscoGLOSSUS*. Thus far I have not been able to obtain this in axolotl. It is of great importance to examine further the nature of the ectodermal proliferations and to find whether indeed the embryo is able to keep the activated ectoderm-growth within bounds by its inductive actions, which the adult organism evidently cannot (or not always) do.

It is very likely that also in normal embryonic development the indifferent material must be activated by factors emanating from its immediate neighbourhood. In the experiment this activation can be performed by various substances. It is as yet an open question which factor in normal development activates the material.

However, even if we should know this, yet the problem of the "organization", the formation of the structures, grouping of cell masses, etc., would not have come much nearer to the solution. In this respect I entirely agree with WEISS <sup>29)</sup>, who critically discussed the "organizer-problem" and sharply formulated the objections, also felt by myself, to the researches on "chemical induction". The above may be a support to his conceptions. I hope that the study of the connection between on the one hand the structure of the cell groups known as organizers (in which I will also include the localization of the various metabolic processes in the organizers) and on the other hand the structure of the induced organ will afford a

<sup>26)</sup> B. I. BALINSKY, Arch. f. Entw.mech. **105**, 718 (1925); **110**, 63 and 71 (1927); **103**, 704 (1933).

<sup>27)</sup> F. G. GILCHRIST, Physiol. Zoology **1**, 231 (1928).

<sup>28)</sup> G. CASTELNUOVO, Bollet. zool. **3**, 291 (1932).

<sup>29)</sup> P. WEISS, Physiol. Reviews (4) **15**, 639 (1935).

better insight into the problem of organization. In this direction I have already previously made attempts. 5, 30) It is to be recommended to continue and extend these researches.

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30) M. W. WOERDEMAN, *Zeitschr. mikr. anat. Forsch.* 36, 600 (1934).

**Physics.** — *On the Structure of Solid Chlorine.* By W. H. KEESOM and K. W. TACONIS. (Abstract of Communication N<sup>o</sup>. 240e from the KAMERLINGH ONNES Laboratory at Leiden).

(Communicated at the meeting of February 29, 1936).

The structure of solid chlorine was determined with the X-ray goniometer with moving film, by irradiating a rotating single crystal of the substance.

From the gnomonic projection we derived a tetragonal structure, with  $\frac{c}{a} = 0,715$ .

For the determination of the absolute dimensions of the unit cell and for the conclusions on the space group we availed ourselves of the data from DEBYE-SCHERRER diagrams made by KÖHLER<sup>1)</sup>.

We found for the unit cell  $a = 8,56 \text{ \AA}$ ,  $c = 6,12 \text{ \AA}$ . We concluded to a space group  $D_4^{1h}$  in which the co-ordinates of the Cl atom are  $x = 0,125$ ;  $y = 0,167$ ;  $z = 0,107$ .

We represent the arrangement of the Cl atoms in fig. 1. It shows a projection of the unit cell on the horizontal plane in the way as done in the International Tables for the Determination of Crystal Structure.

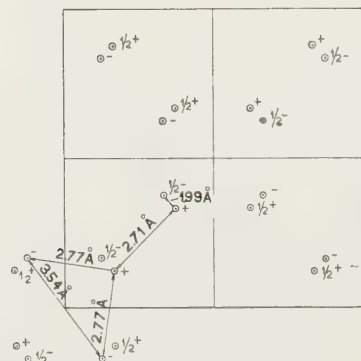


Fig. 1. Structure of solid chlorine.

The distance of the Cl atoms in the molecule in this molecular lattice is 1,99 Å. This value most satisfactorily agrees with  $2 \times$  the value (0,99 Å) given by PAULING<sup>2)</sup> for Cl in his table of the normal electron-pair-bond radii of atoms. The minimum distance between Cl atoms of different molecules in the arrangement mentioned above amounts to 2,71 Å.

<sup>1)</sup> J. W. L. KÖHLER, Thesis, Leiden (1934).

<sup>2)</sup> L. PAULING, *Proc. nat. Acad. U.S.A.* 18, 293 (1932).



**Physics.** — *The mechanism in the positive column of a discharge.*  
By L. S. ORNSTEIN, H. BRINKMAN and T. HAMADA. (Communication  
from the Physical Institute of the University of Utrecht.)

(Communicated at the meeting of February 29, 1936).

SUMMARY.

The measurements by HAMADA<sup>1)</sup> of the temperature  $T$  of the gas along the diameter of a narrow tube, containing the positive column of a discharge in nitrogen, are discussed. The importance of the determination of  $T$  for the mechanism of a gas-discharge is emphasized. It is shown that the velocitydistribution of the electrons, depending on the parameter  $E_0 \cdot \lambda$  ( $E_0$  axial fieldstrength,  $\lambda$  electronic mean free path) varies along the tube-diameter; this variation is only due to the radial variation of  $T$ .

For the discharge in nitrogen the fact is reported that  $E_0 \lambda$  ( $= 0,066$  Volt) is independent on the discharge conditions for pressures between 10 and 30 mm. At lower pressures  $E_0 \lambda$  increases, thus electrons with high energies become more probable.

The different shape of the intensitycurves over the tube-diameter for  $N_2$  and  $N_2^+$  bands are discussed. It is proved qualitatively that the effect of the increase of the total excitationprobability of the  $N_2$  bands with temperature  $T$  (due to the excitation from  $N_2$  molecules in higher vibrational states) must be taken into account in order to explain the experimental facts.

In an appendix an elementary deduction of the velocitydistribution of electrons in a gasdischarge is given.

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In a previous communication<sup>1)</sup> one of us has given a survey of the main results of temperature-measurements in the positive column of a discharge in nitrogen. Together with the theoretical interpretation of these results, we will give in this paper a more general description of the mechanism in the positive column of a discharge.

§ 1. *The temperature of the gas in a discharge.*

In a discharge one of the most important facts to be known is the temperature  $T$  of the gas as a function of the place. If in a cylindrical tube the temperature has a maximum in the axis of the tube, the gasdensity has a minimum. The electrons and ions moving in axial direction, thus have the highest mobility in the axial regions of the tube. So the current-

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<sup>1)</sup> T. HAMADA, Proc. Royal Acad. Amsterdam, **39**, 50 (1936). Determination of the temperature in the column of a discharge from the intensity-measurement of rotational band spectra. — See this paper for experimental details.

density as a function of radius shows a still more prominent maximum than the radial electron distribution does. The radial temperature distribution is therefore strongly related with the so called radial "contraction" of the discharge, an effect that is easily noticed as the gaspressure increases.

Besides in many other aspects the temperature of the gas is of high interest. The phenomena in the discharge in which the mean free path of the particles plays a rôle (diffusion, velocitydistribution of the electrons and excitation of the gas by electrons) depend on the gastemperature; further in the effects depending on the v.d. (velocitydistribution) of the gasparticles, as there are the effectivity for collisions of the second kind, the contribution to the luminosity by thermal excitation of the gas, the widths of spectral lines, etc.

In the figs. 6—12 of T. HAMADA's paper the temperature as a function of radius is shown for a number of pressures and total currents. These functions can be considered as parabolae:

$$T = T_0 - \beta r^2.$$

Near the wall of the tube the measured temperatures may be too high. For it is difficult to determine  $T$  as the  $N_2$ -bands have a low intensity compared with the intensity in the axis of the tube and further, due to the way in which the end-on observations have been performed and measured, the averaging over a certain region of the tube-radius results in a systematic error.

The determination of  $T$  from the intensity-distribution in bandspectra is in our case accurate within 5 %. For this reason, together with the fact that in some cases only a few points fix the curve, the values of  $\beta$ , determining the shape of the radial temperature distribution, are inaccurate. They don't show a well defined dependence upon pressure, currentstrength and watt-input. We can only say that the observed values of  $\beta$  increase with increasing wattinput per cm in the column, in accordance with the theoretical expectation from the energy-equation.

The values of the temperature in the axis,  $T_0$ , are better defined. In fig. 5 of the cited communication of T. HAMADA the linear relation between temperature and the product p.i has been shown. More than this curve

the plot of  $E_0$  ( $E_0$  = fieldstrength in the axis of the tube) against  $\frac{p}{T_0}$  has a direct physical meaning (fig. 1). These curves show the relation between fieldstrength and gasdensity  $\left( \propto \frac{p}{T_0} \right)$ . It suggests the constancy of  $E_0 \lambda \left( \lambda \propto \frac{T}{p}, \text{ the mean free path of the electrons} \right)$  with varying discharge conditions; only at low pressures  $E_0 \lambda$  increases. These results are not in accordance with the relation between  $E_0$  and  $\lambda$  given by GÜNTHER-SCHULZE<sup>2)</sup>.

<sup>2)</sup> A. GÜNTHERSCHULZE, Zs. f. Phys. **41**, 718 (1927); **42**, 763 (1927).

In fig. 2 (upper curve) we plotted the value of  $E_0\lambda$  in electron-Volts as a function of gaspressure. Each value is the mean for all the currents at

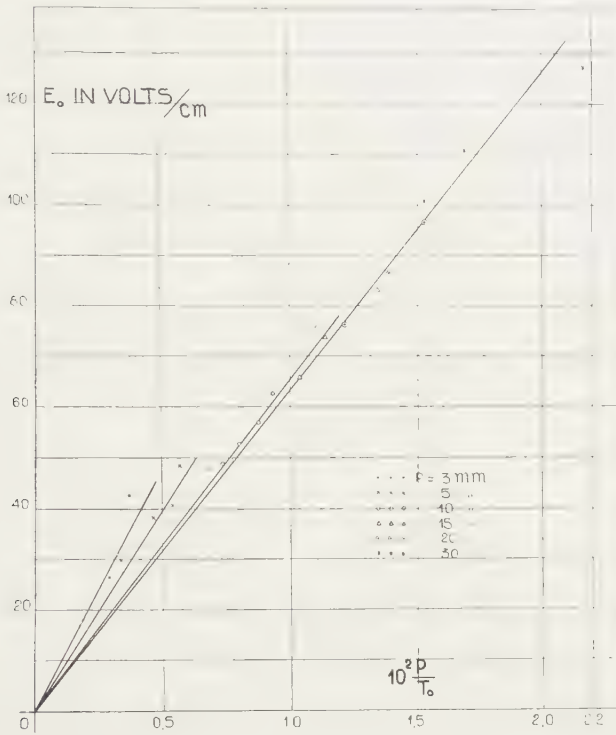


Fig. 1.

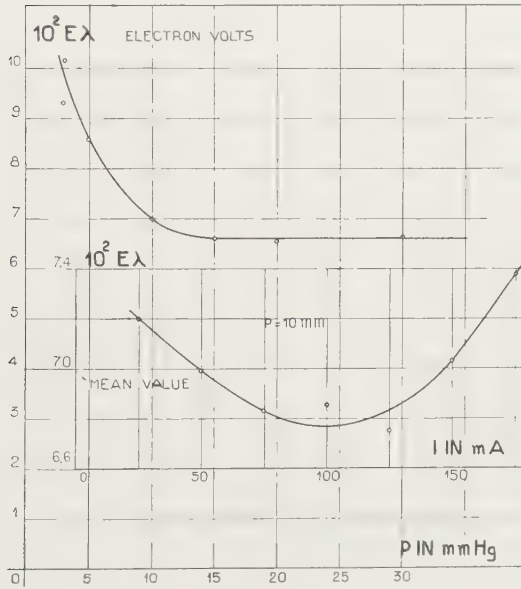


Fig. 2.

which experimental values of  $E_0$  and  $T$  were available.  $E_0\lambda$  for different



currents at constant pressure deviates from the average less than 7 %, except for  $p=3$  mm, in which case  $E_0\lambda$  differs from the mean value + 15.7 %, -8.7 %, -7.0 % for  $i=25, 50$  and  $75$  mA. respectively.

For the calculation of  $E_0\lambda$  we have used as a value for the mean free path of electrons in  $N_2$  at 1 mm. pressure and  $0^\circ\text{C}$   $2.85 \cdot 10^{-2}$  cm. This is a mean value for electrons moving in  $N_2$  with velocities aequivalent with about 5 e.V. <sup>3)</sup>

## § 2. Conclusions about the velocitydistribution (v.d.) of the electrons at different discharge conditions.

The value of  $E_0\lambda$  is the parameter which fix the v.d. of the electrons. In different ways <sup>4)</sup> one can show that the number of electrons having energies between  $\varepsilon$  and  $\varepsilon + d\varepsilon$  is given by

$$n_e(\varepsilon) \cdot d\varepsilon = C \cdot \varepsilon^{1/2} \cdot e^{-a \left(\frac{\varepsilon}{E_0\lambda}\right)^2} \cdot d\varepsilon \quad . \quad . \quad . \quad . \quad (1)$$

$$\left[ a = \frac{3m}{Mq^2}, \quad m = \text{mass of electron}, \quad M = \text{mass of gasparticle}, \right.$$

$$\left. q = \text{electronic charge} \right]$$

assuming only elastic collisions of the electrons with the gasparticles, very small kinetic energies of the gasparticles compared with the energy of the electrons, small  $E_0\lambda$  values ( $E_0\lambda < 1$  Volt),  $\lambda$  independent on the electron velocities and no electrostatic interaction of the electrons among each other.

With this distributionfunction one can prove that the mobility  $\mu$  of the electrons <sup>4)</sup> is given by

$$\mu = \frac{c \cdot \lambda}{\sqrt{E_0\lambda}} \cdot (c = \text{constant}) \quad . \quad . \quad . \quad . \quad . \quad (2)$$

If the excitation and ionisation of the gasparticles is taken into account the above mentioned simple form of the v.d. function alters in a way typical for the gas in question <sup>5)</sup>. But still the value of  $E_0\lambda$  is the most important parameter. Complications arise if the gastemperature  $T$  is so

<sup>3)</sup> R. B. BRODE, Rev. Mod. Phys. **5**, 257 (1933) (fig. 11).

<sup>4)</sup> M. J. DRUYVESTEYN, Physica **1**, 1003 (1934); Physica (old series) **10**, 61 (1930).  
A. M. CRAVATH, Phys. Rev. **46**, 332 (1934).

B. DAVYDOV, Sowj. Phys. **8**, 59 (1935).

P. M. MORSE, W. P. ALLIS and E. S. LAMAR, Phys. Rev. **48**, 412 (1935).

For an elementary deduction of equation (1) see the appendix to this paper.

<sup>5)</sup> M. J. DRUYVESTEYN, Physica **3**, 65 (1936) (Neon).

J. A. SMIT, to be published shortly in Physica (Helium).

high, that the kinetic energy of the gasatoms is not very small compared with the electronenergies<sup>6)</sup> and if the mutual electrostatic interaction of the electrons must be taken into account. In these cases  $E_0\lambda$ ,  $T$  and  $n_e$  determine the v.d. In the nitrogen-tube which T. HAMADA used, we estimate the number of electrons per  $\text{cm}^3$  in the axis of the tube to  $10^{10}$  à  $10^{11}$ . The electrostatic interaction may then be neglected and we assume that in our cases the temperature of the gas doesn't have an appreciable influence on the v.d. of the electrons.

From fig. 2 we may thus conclude that the v.d. in the positive column of the nitrogen-discharge in the axis of the tube is independent on the dischargeconditions at pressures between 10 and 30 mm. At lower pressures the distribution varies in such a way that higher electron-energies become more probable.

In the tube-axis the v.d. seems to be for a certain pressure rather independent on the currentstrength. In the case of 10 mm pressure  $E_0\lambda$  is observed for a large number of currents. In fig. 2 (lower curve, enlarged scale!) is shown that there exists in the tube axis a small variation of the v.d. with current.

### § 3. *The variation of the electronic v.d. along the diameter of the cylindrical discharge.*

As the temperature of the gas falls down towards the wall of the tube we see that  $E_0\lambda$  decreases along the tube-radius proportional to  $T$ . Thus the v.d. of the electrons differs for the various cylindric zones of the tube in such a way that high velocities are more probable in the axis of the tube than in the layers near the wall.

On the first sight against this conclusion may be objected that outside the tube-axis a radial component of the field  $E_r$  exists and the total field  $E = \sqrt{E_0^2 + E_r^2} > E_0$ . Qualitatively we shall show, however, that for the electronic v.d.  $E_0\lambda$  is the determining parameter and not  $E\lambda$ .

According to SCHOTTKY<sup>7)</sup> the radial field  $E_r$  has such a value that the mean driftvelocity of the electrons in radial direction, due to the combined influences of diffusion towards the wall and radial field action, equals the mean radial driftvelocity of the positive ions.

The radial force acting on the electrons is therefore:

$$-E_r e - \frac{d}{n_e} \frac{dn_e}{dr} \quad (3),$$

the two components of the force acting in opposite directions.

<sup>6)</sup> B. DAVYDOV, l.c. and SMIT's paper.

<sup>7)</sup> W. SCHOTTKY, Phys. Z.S. **25**, 342, 635 (1924).

M. J. DRUYVESTEYN, ZS. f. Phys. **81**, 571 (1933).

<sup>7a)</sup>  $d(\cdot) E_0\lambda$  can be calculated from equation (1).

Between two successive collisions the electron moves in a field of strength  $E = \sqrt{E_0^2 + E_r^2}$ . However, the stationary v.d. is determined after a great number of collisions, that means, depends on the balance of energy-yields and energy-losses. This balancing differs strongly from the case in which no radial diffusion, caused by the radial variation of the electronconcentration, exists and only an electric field is present. For in our case, due to the radial diffusion, the number of energy-losses is larger than the number of energy-yields and the effect of an  $E$  larger than  $E_0$  is compensated.

Quantitatively the influence of the radial field and electron diffusion on the v.d. may be calculated on the basis of the fundamental equation of LORENTZ<sup>8)</sup>, extended by the work of MORSE, ALLIS and LAMAR<sup>4)</sup>. From LORENTZ's equation<sup>8)</sup> one directly sees that the variation of the electron v.d. depends on the value of the force acting on an electron (see our expression (3)) and the value of  $E_r$  is just so that this force is very small compared with  $e \cdot E_0$ .

A simple and more general proof, that the v.d. of electrons is the same if  $E_0\lambda$  remains constant, is as follows. Assuming that the electrical energy-input per element of volume is totally given to the gas by the collisions of electrons with gasparticles, we can write:

$$E_0 \cdot I = \gamma \cdot n_e n$$

[ $I$  = current density,  $\gamma$  is a function of the v.d. of the electrons,  $n$  = number of gasparticles per  $\text{cm}^3$ ].

Now we know:

$$I = n_e \cdot e \cdot \mu \cdot E$$

( $e$  = electronic charge)

$$\mu = \frac{c \cdot \lambda}{\sqrt{E_0 \lambda}}$$

$$\lambda = \frac{1}{n \cdot Q}$$

( $Q$  = total crosssection of the gasparticles for collisions with electrons). Thus we have:

$$(E_0 \lambda)^{3/2} = \frac{\gamma}{Q \cdot e \cdot c}.$$

If the v.d. doesn't vary, then we find  $E_0\lambda$  is constant.

Conclusion: *The temperature variation over the tube-diameter is the only reason for the radial variation of the velocity distribution of the electrons.*

<sup>8)</sup> H. A. LORENTZ, Theory of Electrons (1909, Teubner) page 266—274; see equation (65).



#### § 4. *The excitation of the molecular spectra in the discharge.*

We shall try to give the interpretation of the curves, giving the intensity of a negative and a positive band of  $N_2$  as a function of the radius. In fig. 13 of HAMADA's paper such curves are given. The intensity scale for these curves, obtained with various currents, must be adjusted in such a way that (— as has been proved by further experiments —) the intensity in the tube-axis is proportional to the current. This holds as well for the  $N_2^+ 0-0$  band ( $\lambda 3914 \text{ \AA}$ ) as for the bands  $0-3$  ( $\lambda 4059$ ) and  $1-4$  ( $\lambda 3998$ ) of the second positive bandsystem of  $N_2$ . From fig. 2 we have seen the small variation of the electronic v.d. in the tube-axis with current. Thus the currentdensity in the axis is practically proportional with the number of electrons. It is not exact to conclude that thus the intensity is proportional to  $n_e$ , for the function giving the currentdensity at various radii may differ for different currents. The latter may occur, as the temperatures along the radius are different for different currents (see fig. 9 in HAMADA's paper). However, probably the conclusion that the intensity is proportional to the number of electrons is correct.

From the detailed study of the excitation conditions in a discharge<sup>9)</sup>, one can predict that for the rather high pressures with which we are dealing, the intensity of  $N_2$  and  $N_2^+$  bands (assuming excitation directly from the fundamental level of  $N_2$ ) is independent on the pressure (as has been checked experimentally by T. HAMADA) and proportional to the number of electrons. Using the notation giving in the cited articles<sup>9)</sup> the number of excited particles

$$n_a = \frac{\alpha_e}{\beta} \cdot n_e,$$

$$\alpha_e = \int_{\sqrt{\frac{2\varepsilon_a}{m}}}^{\infty} v \cdot q(v) \cdot f(v) \cdot dv \quad \text{and} \quad \beta = \int_0^{\infty} V' \cdot Q'(V') \cdot F(V') \cdot dV'$$

$\varepsilon_a$  = energy of the excited state,

$f(v)$  is the distribution function for the electronvelocities,

$q(v)$  the excitation function of the nitrogen bands<sup>10)</sup> in question,

$F(V')$  is the distribution function for the relative velocities of the gas-particles,

$Q'(V')$  the crosssection of the molecules for a collision of the second kind.  
We see that  $\beta$  depends on the temperature of the gas.

<sup>9)</sup> L. S. ORNSTEIN and H. BRINKMAN, *Physica* **1**, 797 (1934).

P. J. HARINGHUIZEN, Thesis, Utrecht (1935).

<sup>10)</sup> L. S. ORNSTEIN u. G. O. LANGSTROTH, *Proc. Royal Acad. Amsterdam*, **36**, 384 (1933).

G. O. LANGSTROTH, *Proc. Roy. Soc. London*, **146**, 166 (1934); **150**, 371 (1935).

O. HERRMANN, *Ann. d. Phys.* **25**, 166 (1936).

In molecular spectra the intensity of one band is the total intensity of all rotational lines together.

In the investigation of the excitation of molecular spectra we must account for the following effect. If the temperature of the gas rises, the population of the higher vibrational states of the  $N_2$  molecule (in the fundamental  $^1\Sigma$ -state) increases. At  $1500^\circ\text{K}$  the ratio of the number of molecules in the vibrational state with quantumnumber 0 to the number of molecules in the vibrational state with quantumnumber 1 evaluates  $\frac{1}{10}$ . If the excitationprobability from the 0-state is small compared with the excitationprobability from the 1-state the total excitationprobability turns out to increase with the temperature of the gas! This is the case for the bands of the second positive bandsystem of  $N_2$ . That can be seen directly from the relative position of the molecular-potential curves on the nuclear-distance scale<sup>11)</sup>, together with the application of the FRANCK-CONDON-principle for excitation<sup>10)</sup>. For the  $N_2^+$  band this effect does not occur. In both cases no calculations of excitationprobabilities from higher vibrational states have been carried out; so we cannot calculate the magnitude of this effect. It is very probable that the relation between intensity and current for the positive bands is affected by the reported phenomena.

In the case of 10 mm pressure the intensitydistribution along the diameter of the tube has been measured for the band  $\lambda 3914$  of  $N_2^+$  as well as for the band  $\lambda 3998$  of  $N_2$ . The ratio of the intensity of the  $N_2$  band and of the  $N_2^+$  band shows a maximum near the tube axis (see fig. 3; computed

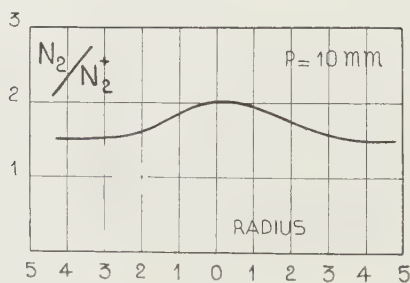


Fig. 3.

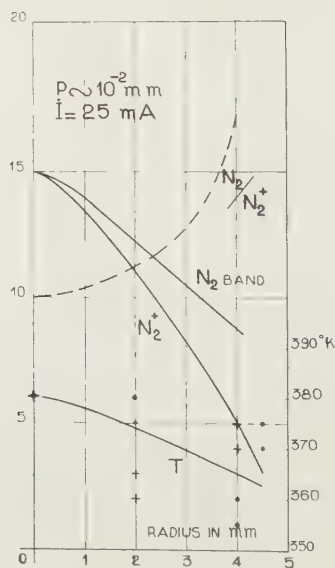


Fig. 4.

from fig. 13 in HAMADA's paper). As we have seen the v.d. of the electrons shifts to the lower velocities if we go from the axis towards the wall. Thus

<sup>11)</sup> W. JEVONS, Report on Bandspectra (1932).

the remarkable way in which the intensity ratio of positive and negative bands varies with the radius can only be understood if the effect of the variation of the v.d. is more than compensated by the effect of the increase of the total excitationprobability with increasing gastemperature.

For the very low pressure of about  $10^{-2}$  mm ( $\lambda$  about 4 cm; in this case SCHOTTKY's theory is not valid), the experimental facts are quite different from the case stated above. It has been found by HAMADA (see fig. 12 of his paper) that the temperature is practically constant over the tube-diameter. The small temperature variation in radial direction is shown on larger scale in our fig. 4 (• •  $T$  derived from  $N_2^+$  band, ++  $T$  derived from  $N_2$  band). Thus there will be a radial variation of the v.d. of the electrons. As the temperatures are low the total excitationprobability for the  $N_2$  band is the same at different radii. The intensity ratio of  $N_2$  and  $N_2^+$  bands has in this case a minimum at the tube-axis and increases with 70 % near the wall of the tube, indicating the variation of the electron v.d. along the diameter.

## APPENDIX.

### *Elementary deduction of the v.d. of electrons moving in a gasdischarge with a constant gradient.*

The following elementary deduction of the velocitydistribution law is perhaps of some interest as this law is of utmost importance for the investigation of the discharge.

We assume that the mass  $M$  of the atoms (or molecules) is very large in comparison to that of the electrons, so that  $\frac{m}{M}$  may be considered as small compared to unity. Further we assume that the velocity of the atoms is small (low temperature of the gas). The electrons move in an electric field of strength  $E$ . Under these assumption the energy of the electrons is changed by the field between the collisions with the atoms in positive or negative sense, and this energy is changed after each collision in the average with the factor  $1 - \frac{2m}{M} = 1 - \beta = \alpha$ .

As a first approximation the distribution law shows a spherical symmetry.

Let us now follow an electron on its way during  $n$  free paths ( $n-1$  collisions) and let  $l_1, l_2, \dots, l_n$  be the successive paths between the collisions, which form angles  $\vartheta_1, \vartheta_2, \dots, \vartheta_n$  with the direction of  $E$ . Let the energy at the beginning of the path be  $\varepsilon_0$ , than we have:

$$\varepsilon_n = (\dots [(\varepsilon_0 + Eel_1 \cos \vartheta_1) \alpha + Eel_2 \cos \vartheta_2] \alpha + Eel_3 \cos \vartheta_3] \alpha + \dots \\ \dots) \alpha + Eel_n \cos \vartheta_n$$

or

$$\varepsilon_n = \varepsilon_0 \alpha^{n-1} + Ee \cdot [l_1 \cos \vartheta_1 \cdot \alpha^{n-1} + l_2 \cos \vartheta_2 \alpha^{n-2} + \dots + l_n \cos \vartheta_n] \quad (I)$$



The mean value of  $\varepsilon_n$  will therefore be:

$$\frac{\varepsilon_n}{\varepsilon_0} = \alpha^{n-1}$$

as the mean value  $\overline{\cos \vartheta} = 0$ . After a very large number of collisions the particle, with initial energy  $\varepsilon_0$ , has the energy 0.

Let us now determine  $\overline{\varepsilon_n^2}$ ; for this quantity we get:

$$\varepsilon_n^2 = \varepsilon_0^2 \alpha^{2(n-1)} + E^2 e^2 \cdot [l_1^2 \cos^2 \vartheta_1 \cdot \alpha^{2(n-1)} + \dots + l_n^2 \cos^2 \vartheta_n]$$

as

$$\overline{\cos \vartheta_p \cdot \cos \vartheta_q} = 0 \quad (p \neq q).$$

Now  $\overline{l_1^2 \cos^2 \vartheta_1} = \frac{2\lambda^2}{3}$ , where  $\lambda$  means the mean free path of the electrons. Thus we get:

$$\begin{aligned} \overline{\varepsilon_n^2} &= \varepsilon_0^2 \alpha^{2(n-1)} + \frac{2E^2 e^2 \lambda^2}{3} \cdot \frac{1 - \alpha^{2n}}{1 - \alpha^2} \\ &= \varepsilon_0^2 \cdot \alpha^{2(n-1)} + \frac{E^2 e^2 \lambda^2 M}{6m} \cdot (1 - \alpha^{2n}) \end{aligned}$$

for very large values of  $n$  we find:

$$\overline{\varepsilon^2} = \frac{E^2 e^2 \lambda^2 M}{6m}.$$

Now the change of the energy distribution of the electrons is given by a generalised diffusion equation (PLANCK-FOKKER) in which  $\overline{\beta \varepsilon_n^2}$  ( $n \rightarrow \infty$ ) is the diffusion constant. This can be proved taking (I) as an EINSTEIN-LANGEVIN equation of the form

$$\frac{d\varepsilon}{dn} = -\beta \varepsilon + F^*), \quad \beta = \frac{2m}{M}$$

and deriving the diffusion equation in the common way. The distribution in energy is then a GAUSSIAN distribution with modulus  $2\overline{\varepsilon^2}$ ; however, taking into account that for a given energy the velocity can have any direction with the same probability, we find for the velocitydistribution equation (1) of this paper.

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\*) Compare: G. E. UHLENBECK and L. S. ORNSTEIN, On the theory of the BROWNIAN Motion, Phys. Rev. **36**, 823 (1930). See especially §§ 5 and 6.

**Physics.** — *Change of the dipole moment of transformeroil by the alteration in practice.* By L. S. ORNSTEIN, D. TH. J. TER HORST and G. H. FREDERIK. (Communication from the Physical Institute of the University of Utrecht).

(Communicated at the meeting of February 29, 1936).

### *Summary.*

It is proved that the mean dipole moment of the substances of the oil increases by alteration of transformeroil. In order to do this the electrical polarization has been measured as function of temperature, as pointed out by DEBYE.

ORNSTEIN, JANSSEN, KRIJGSMAN and TER HORST have shown that the change in insulating qualities of transformeroil in practice must be caused by reactions with oxygen from the air<sup>1</sup>). If, however, the oxygen oxidizes the higher hydrocarbons of transformeroils, there must be a change in dipole moment as function of the time of alteration. By measuring this change in dipole moment we are able to follow the rate of oxidation.

The method used for measuring the dipole moment is the same as used by HIDDINK<sup>2</sup>), who followed the variation in electrical polarization as function of temperature.

The electrical polarization is in accordance with DEBYE's theory<sup>3</sup>) a linear function of the reciprocal value of the absolute temperature;

$$\frac{\varepsilon - 1}{\varepsilon + 2} \frac{M}{\rho} = \frac{4\pi}{3} N \left[ a_0 + \frac{\mu^2}{3KT} \right]$$

where  $\varepsilon$  the dielectric constant,

$M$  the molecular weight,

$\rho$  the density,

$N$  the number of Avogadro,

$a_0$  the polarization caused by the electrons removed in the electric field,

$\mu$  the dipole moment,

$K$  the BOLTZMANN constant,

$T$  the absolute temperature.

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1) L. S. ORNSTEIN, C. JANSSEN Czn., C. KRIJGSMAN and D. TH. J. TER HORST, *Physica* II, 201 (1935).

L. S. ORNSTEIN, C. JANSSEN Czn. and C. KRIJGSMAN, *Arch. f. Elektrotechnik*, 27, 489 (1933).

2) J. L. HIDDINK, Thesis, Utrecht (1932).

3) P. DEBYE, *Polare Molekeln*, Leipzig (1929).

It is proved by GINSEL (results not published) and by HIDDINK <sup>1)</sup> that the mean molecular weight of transformeroil is about 250. For the density  $\rho$  we take the measured density of the oil. In this way we can find a mean dipole moment of the substances in the transformeroil.

In fig. 1 we have plotted the quantity  $\frac{\varepsilon - 1}{\varepsilon + 2} \frac{M}{\rho}$  as function of  $\frac{1}{T}$ . There is corrected for the variation with temperature of  $\rho$ .

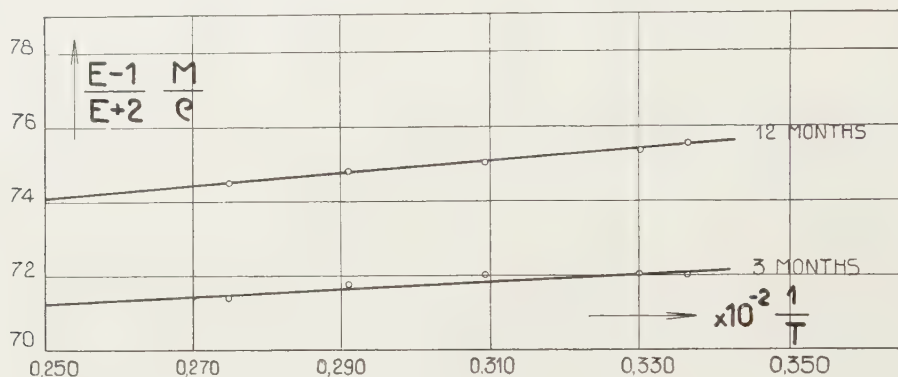


Fig. 1.

We measured two probes which have been altered resp. for 3 and 12 months in a transformer <sup>2)</sup>.

From the figure we see that the probe "3 months" has a mean dipole moment  $\mu = 0.41 \cdot 10^{-18}$  e.s.u. and the probe "12 months" has a mean dipole moment  $\mu = 0.52 \cdot 10^{-18}$  e.s.u.

These preliminary results show the possibility to follow the oxidation-processes in transformeroil by measuring the variation of the mean dipole moment as function of the alteration time. It is thus possible to measure the rate of oxidation by an electrical method.

It might be important to point out that one is able to follow chemical reactions measuring the dipole moment as function of time.

Further results on this subject will be published.

<sup>1)</sup> J. L. HIDDINK, loc. cit.

<sup>2)</sup> The oil used was one of the oils altered in a transformer by ANDERSON, Vesteras, Sweden. Compare: Conférence Internationale des Grands Réseaux Électriques à Haute Tension, Paris (1935).



**Physics.** — *An Eighth Isotope of Molybdenum.* By J. DE GIER and P. ZEEMAN.

(Communicated at the meeting of February 29, 1936).

The method of the carbonyls being applied with good results to *Ni* and *Fe*<sup>1)</sup> was also successful with Molybdenum. A new isotope of mass number 102 was discovered, the number of isotopes of *Mo* now being no less than eight.

The first attempts made by ASTON according to the method of accelerated anode rays were unsuccessful. Later on ASTON<sup>2)</sup> obtained a sample of the carbonyl of molybdenum and now seven isotopes were found.

Photometry of the group was not easy, the total intensity being spread over seven almost equally intensive components. So the lines had to be photographed in a position of the plate giving less than normal resolution. The results which, according to ASTON, must be taken as provisional only were:

Mass numbers: 92, 94, 95, 96, 97, 98, 100.

% abundance: 14.2, 10.0, 15.5, 17.8, 9.6, 23.1, 9.8.

Our experiments were also made with the hexacarbonyl. A free sample was sent to us by the I. G. Farben Industrie at Frankfurt. We are very grateful for this generous gift, which made the present experiments possible.

The vapour pressure of the white crystalline powder was just high enough for the sample to be used in the common way. As with *Ni* and *Fe* carbonyl, we were forced to admix a quantity of oxygen.

This time the percentage of  $O_2$  amounted to fifty and more. Otherwise a coating of *Mo* would have been formed on the inner wall of the discharge tube.

Such a metallic mirror in the cathodic region soon disturbed the discharge and the bundle became deflected in a short time. When mixing the carbonyl with some fifty percent of oxygen, the tube could be held in a steady state during several exposures. But by doing so, the intensity of the *Mo* lines was appreciably reduced. Moreover, a carbonyl molecule contains as much as six CO-groups. So we were obliged to use wide canals to obtain a sufficient intensity for the *Mo* parabolas.

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1) J. DE GIER and P. ZEEMAN, Proc. Royal Acad. Amsterdam, **38**, 810, 959 (1935).

2) F. W. ASTON, Proc. Roy. Soc. **130**, 308 (1931).

Of course wide canals impair the sharpness of the parabolas. By so doing, the lines were never totally resolved. For this reason an estimation of the intensities was almost impossible.

These difficulties made it very hard to obtain a plate good enough for reproduction. When the time of exposure was short, the faint line 102 did not appear. With a much longer time of exposure the whole group of seven intensive isotopes formed a black cluster and the new isotope was apt to disappear in the diffuse background of the cluster. Many plates were used before a small number was obtained that more or less satisfied the conflicting requirements.

The reproduction of one of these plates will clearly show all of the seven well-known isotopes.

At the same time the intensity is just great enough to show isotope 102 as a faint line. In the reproduction a trace of it is still visible.

ASTON reported on his trouble with the doubly ionized *Hg* atoms. This group just falls in the region of *Mo* lines. So we took precautions to reduce the *Hg* vapour-pressure in the tube. Although a slight mercury vapour from the diffusion pumps is frequently unavoidable, we obtained several plates on which the *Hg* parabolas could not be found.

Other plates only revealed the primary *Hg* line having little or no prolongation towards the magnetic axis, indicating that the parabolas of the second order were not to be feared. Exposures without carbonyl confirmed this conclusion.

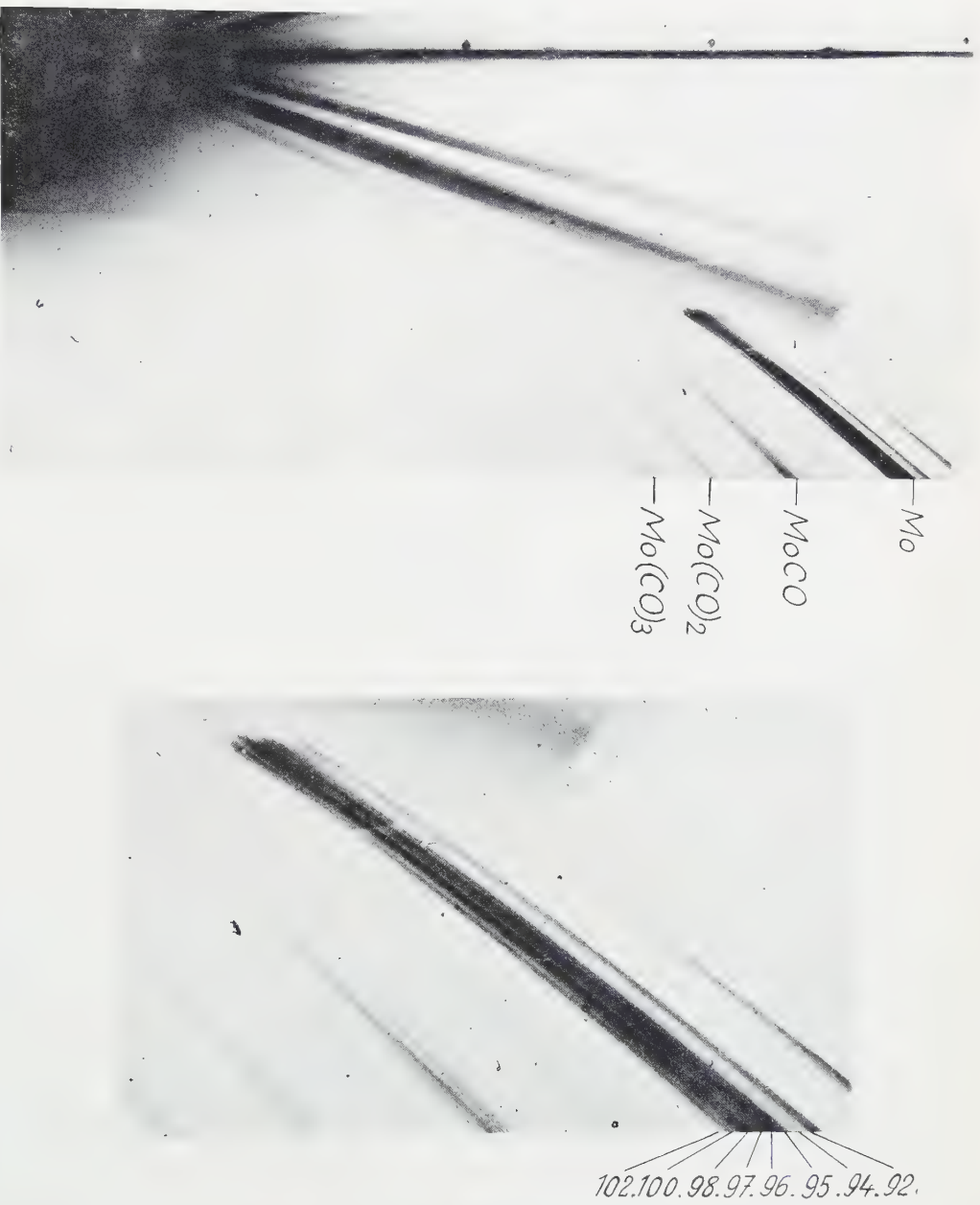
In the reproduction several carbonyls of *Mo* will be seen, such as  $\text{MoCO}$ ,  $\text{Mo}(\text{CO})_2$ . On more intensive plates all the compounds up to  $\text{Mo}(\text{CO})_6$  could be distinguished, though with decreasing intensity where the number of  $\text{CO}$ -groups increased.

On the original plate and a few others faint lines could be detected for  $^{102}\text{MoCO}$  and even a shadow of line  $^{102}\text{Mo}(\text{CO})_2$  was discovered. A confirmation of our explanation about the identity of the new line was also found in the prolongation of the parabolas to the magnetic axis. The isotopes already known very frequently showed that phenomenon. A slight prolongation of  $^{102}\text{Mo}$ , however, was also discovered on the most intensive plates.

It will be apparent that no good estimation of the relative abundance of the isotope could be given. The neighbouring isotope 100 was never quite free from the most intensive line 98. A reliable figure was not attainable. A provisional comparison led to about 2—3 % of the total.

Several isotopes of *Mo* have the property of being isobaric with isotopes of elements in the same region of the isotopic table. As ASTON pointed out,  $^{96}\text{Mo}$  forms the lightest isobaric triplet with the zirconium isotope  $^{96}\text{Zr}$  and the Ruthenium isotope  $^{96}\text{Ru}$ .

In the same way the next triplet is now formed by  $^{102}\text{Mo}$  being isobaric with  $^{102}\text{Ru}$  and  $^{102}\text{Pd}$ . Further  $^{92}\text{Mo}$  and  $^{94}\text{Mo}$  are isobaric with







$^{92}\text{Zr}$  and  $^{94}\text{Zr}$  respectively. Finally  $^{98}\text{Mo}$  will form a doublet with the uncertain  $^{98}\text{Ru}$  isotope.

$^{102}\text{Mo}$  is also of some interest as to the limitation of the number of isotopes of the elements with even atomic number.

MATTAUCH<sup>1)</sup> decided upon three limits in different regions of the isotopic table.

These limits, as SITTE<sup>2)</sup> pointed out, are somewhat artificial. MATTAUCH looked for the element with the greatest number of isotopes in a certain region on the table and supposed the neighbouring elements would behave in exactly the same manner.

SITTE proposed a more conceivable limitation on referring to GAMOW's general conceptions of the binding energy of the core<sup>3)</sup>. An energy valley is present in which the stable isotopes take their places.

In this way SITTE's limitation enabled him to predict a number of undiscovered isotopes which were mainly the same as those of MATTAUCH.

In some places, however, new isotopes seemed probable, in others MATTAUCH's isotopes became unlikely.

In the case of  $\text{Mo}$ , SITTE predicted  $^{102}\text{Mo}$  where MATTAUCH decided upon  $^{90}\text{Mo}$ . We looked for the latter, but even on the most intensive plates we could not find the slightest trace of it.

In this connection it may be of some interest to record our experiments with krypton and xenon. MATTAUCH predicted an isotope of krypton of mass number 88. Our experiments last year never revealed such an isotope.

From the curve of minimum energy SITTE concludes the isotope to be improbable.

No further isotopes of xenon were predicted. A greatly prolonged investigation did not lead to new results. We only found that the faint isotopes  $^{124}$  and  $^{126}$  were not equally abundant. The latter seemed about half as strong as the former.

*Laboratory „Physica” of the University  
of Amsterdam.*

February 1936.

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1) J. MATTAUCH, *Zeitschr. f. Phys.* **91**, 361 (1934).

2) K. SITTE, *Zeitschr. f. Phys.* **96**, 512 (1935).

3) G. GAMOW, *Zeitschr. f. Phys.* **89**, 593 (1934).

**Hydrodynamique. — Cavitation et Tension superficielle, II.** Par F. K. TH. VAN ITERSON.

(Communicated at the meeting of January 25, 1936).

Pour bien comprendre le phénomène de cavitation, suivons maintenant une seule bulle microscopique dans son mouvement le long de la paroi, dans la couche limite, et prenons pour exemple le tuyau convergent-divergent de la figure 10.



Fig. 10. Bulles d'air s'avancant dans la couche limite d'un tuyau convergent-divergent. A l'endroit indiqué par un point la bulle disparaît brusquement.

L'eau étant saturée d'air à la pression atmosphérique, les bulles sont engendrées dans la couche limite, en une région locale où la dépression devient au moins égale à une demi atmosphère dans le cas de l'eau pure. A leur naissance elles ont un diamètre de 0.6 microns par exemple.

En s'approchant du col, la dépression augmente. Si l'on aurait une seule petite bulle se déplaçant lentement dans la couche limite toujours environnée d'eau saturée d'air à la pression atmosphérique, on pourrait appliquer la formule:

$$r = \frac{2\gamma}{\Delta p}.$$

$\Delta p$  étant la dépression.

Alors la formule indique que dans le col où  $\Delta p$  est la plus grande la bulle devient plus petite qu'à sa naissance, puis le col passé  $\Delta p$  diminue,  $r$  augmente, devient  $\infty$  pour  $\Delta p = 0$ . Puis quand la pression de l'eau surpasse la pression atmosphérique le rayon devient  $r = -\infty$ . La loi de l'équilibre exige donc que pour une dépression infinitésimale le rayon des bulles soit infiniment grand et que pour une légère surpression les bulles soient résorbées.

Naturellement le phénomène ne se passe pas ainsi. L'eau ne contient que 2 % de son volume d'air en saturation. Quand la pression diminue jusqu'à provoquer la naissance spontanée des bulles, celles-ci naissent en si grand nombre que l'air se dégage de l'eau. Ces bulles ne peuvent donc pas grossir démesurément, quand la dépression diminue. Cela pourrait seulement être le cas pour une petite bulle dans de l'eau toujours saturée d'air. En réalité



il se forme une espèce de mousse dans la couche limite et l'air n'est pas supplée<sup>1)</sup>).

Il ne nous est pas possible de poursuivre mathématiquement le changement en diamètre des bulles d'air se déplaçant dans la couche limite et qui diminuent, puis grossissent par diffusion d'air à travers l'eau.

Nous passons donc cette période de changement très limitée des diamètres des bulles pour nous occuper du problème aussi intéressant que la naissance des bulles, celui qui domine la destruction de nos parois métalliques, la disparition quasi-spontanée des bulles au moment que

$$p_{\text{extérieure}} \equiv 1 \text{ atm.} - \frac{2\gamma}{r}.$$

Nous allons calculer la vitesse de contraction d'une bulle et le temps qu'elle met à disparaître à partir du moment où son équilibre est rompu.

Nous négligeons la vitesse de contraction à cet instant, vitesse initiale, qui est encore très faible.

Nous supposons également que l'air ne présente aucune résistance à la résorption.

Cette hypothèse nous paraît admissible, car, au dernier instant de son existence, quand la pression dépasse toute limite, le dernier résidu de bulle d'air est absorbé instantanément. Surtout parce que la surface est très étendue comparée au contenu de la bulle.

Soient:  $s$ , le poids spécifique du liquide,

$g$ , l'accélération due à la pesanteur, et considérons les notations de la figure: l'énergie cinétique de toute la masse d'eau en contraction entourant la bulle est:

$$A = \int_{r_1=r}^{r_1=\infty} \frac{4\pi r_1^2 \cdot s}{2g} \left( v \cdot \frac{r^2}{r_1^2} \right)^2 dr_1 = \frac{2\pi \cdot s}{g} v^2 \cdot r^3.$$

Nous appliquons ici la relation:  $dA = \frac{1}{2} dm \cdot v^2$

et l'équation de continuité:  $4\pi r^2 \cdot v = 4\pi r_1^2 \cdot v_1$

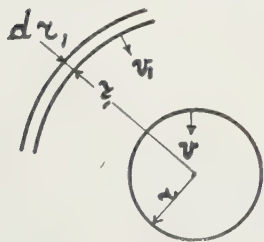


Fig. 11. Contraction concentrique d'une bulle.

Soit  $r$  le rayon de la bulle à l'instant où la contraction brusque commence et supposons que l'accélération soit uniquement due à la contraction par la tension superficielle.

En fait, il y a un phénomène superposé qui agit dans le même sens et sur lequel nous reviendrons plus loin. Il est d'ailleurs de moindre importance au point de vue des surpressions.

Nous pouvons alors écrire que la variation d'énergie cinétique est égale à la variation d'énergie

<sup>1)</sup> En soulageant la pression dans l'eau contenant de l'air en surpression, on peut se former une idée de la génération des bulles et se rendre compte qu'elles naissent toutes au même diamètre. Mais en peu de temps une irrégularité dans la grosseur se produit. Des bulles grandissent aux dépens des autres. Celles-ci, réduites à un certain diamètre de quelques microns s'écroulent.

potentielle mise en liberté par la diminution de la surface (variation d'énergie capillaire):

$$4\pi (r_0^2 - r^2) \gamma = \frac{2\pi s}{g} v^2 r^3$$

$$v^2 = \frac{2g\gamma}{s} \frac{r_0^2 - r^2}{r^3}.$$

On voit que la vitesse de contraction devient infiniment grande lorsque le rayon de la bulle tend vers zéro, car:

$$v = \infty \quad \text{pour} \quad r = 0.$$

Combien de temps met la bulle pour se contracter en passant du rayon  $r_0$  au rayon  $r=0$ :

Nous avons:

$$v = \frac{dr}{dt} = \sqrt{\frac{2g\gamma}{s} \frac{r_0^2 - r^2}{r^3}}$$

$$\frac{d\frac{r}{r_0}}{dt} = \sqrt{\frac{2g\gamma}{s r_0^3} \frac{1 - \left(\frac{r}{r_0}\right)^2}{\left(\frac{r}{r_0}\right)^3}}.$$

Posons  $\frac{r}{r_0} = \sin \varphi$

$$t = \sqrt{\frac{r_0^3 s}{2g\gamma}} \int_{\varphi = \frac{\pi}{2}}^{\varphi = 0} \sin \varphi \sqrt{\sin \varphi} d\varphi = 0,873 \sqrt{\frac{r_0^3 s}{2g\gamma}}.$$

L'énergie potentielle libérée, puis transformée en énergie cinétique, et enfin absorbée en choc, est:

$$A = 4\pi r_0^2 \gamma, \text{ en grammes } \times \text{ cm.}$$

Pour des bulles de différents rayons

$$r = 0,005 \quad r = 0,001 \quad r = 0,0005 \quad r = 0,0003 \text{ cm.}$$

le temps de contraction est:

$$t = \frac{2,54}{10^5} \quad t = \frac{2,28}{10^6} \quad t = \frac{0,803}{10^6} \quad t = \frac{0,38}{10^6} \text{ sec.}$$

Une bulle, qui au moment critique, a 10 microns de diamètre, disparaît en  $\frac{8}{10^7}$  seconde. Entraînée en plein courant, avec une vitesse de 12,5 m/sec., elle parcourt donc 1/100 mm.

6. *Influence de l'huile sur la variation de tension capillaire  
des bulles d'air avec l'eau ou avec le métal: huile,  
catalyseur de cavitation.*

Récemment, on nous avait soumis le problème suivant: Quatre puissantes pompes centrifuges (en bronze), essayées en Hollande, avaient accusé un bon fonctionnement, alors qu'elles cavaient terriblement à Curaçao où elles étaient utilisées à pomper de l'eau de mer pour une distillerie de pétrole de la Cie Royale néerlandaise.

Nous fûmes amenés à imputer ce mauvais fonctionnement à de l'eau contaminée d'huile. Quelques essais de laboratoire nous montrèrent que par addition d'huile Diesel, le débit des tuyaux convergents-divergents est augmenté et la cavitation favorisée par cet élément „catalyseur” de la cavitation.

Quelle est donc l'influence de l'huile? En premier lieu, comme les essais le montrent, la tension superficielle de l'eau avec l'air est beaucoup diminuée par l'huile, mais il y a plus.

On est tenté de croire que les bulles d'air ne s'attachent pas à la surface du verre ou des métaux mouillés si les parois sont absolument propres; il en résulte alors que les bulles ne peuvent pas se former, comme nous l'avons exposé pour les récipients d'ébullition.

En d'autres termes, la présence de l'huile dans l'eau et le long des parois a un double effet, celui de diminuer la tension superficielle de l'air avec l'eau, et d'augmenter celle de cet air avec les surfaces grasses. Ces deux effets sont de même sens, car ils concourent tous deux à une affinité plus grande de l'air avec les surfaces qu'avec l'eau.

On trouve, dans les tables de LANDOLT et BÖRNSTEIN, pour l'angle de capillarité entre air et verre (en présence de l'eau)  $4^{\circ}$  à  $6^{\circ}$ ; c'est peu, mais c'est en suffisant pour fixer les bulles microscopiques d'air à la paroi dans la couche limite.

Avec du cuir mouillé, matière qui résiste bien à la cavitation, les globules d'air ne s'attachent pas (pas d'affinité air-cuir mouillé).

Aussi, pour cette raison, le cuir mouillé est-il utilisé pour les robinets domestiques.

Il est possible que les métaux purs humectés n'ont également pas d'angle de capillarité avec l'air et que celui-ci ne peut s'y attacher.

La figure 12 représente une photographie prise à l'aide du microscope d'une bulle d'un demi millimètre de diamètre adhérente dans de l'eau à la surface polie d'acier, nettoyée avec de l'alcool. L'angle de capillarité est de  $22\frac{1}{2}^{\circ}$ .

Le phénomène devient différent quand le métal est gras. Or, l'eau des turbines hydrauliques, des machines élévatoires, l'eau de sillage des bateaux est toujours souillée par des traces d'huile pour lesquelles les parois métalliques ont une grande affinité et les bulles d'air y adhèrent fortement.

La figure 13 est la photographie d'une bulle d'air d'un demi millimètre



adhérente à la surface d'acier poli graissée d'un peu de vaseline. L'angle de capillarité est de  $90^\circ$ ; la bulle a exactement la forme d'une demi sphère. C'est ainsi qu'on doit se représenter les bulles se déplaçant dans la couche limite.



Fig. 12. Photographie d'une bulle d'air adhérente à la surface propre d'acier poli.



Fig. 13. Photographie d'une bulle d'air adhérente à la surface d'acier poli, graissée avec de la vaseline.

Il faut ajouter pour être plus complet, que l'angle de capillarité est plus grand quand les bulles se contractent que quand elles se délatent. Les bulles représentées venaient de se délater.

7. *Suppressions locales considérables consécutives à la contraction soudaine (écroulement) des bulles d'air: leur effet d'érosion sur les parois.*

Toutes les globules naissent dans la couche limite. Beaucoup d'entre elles sont entraînées et s'écroulent en plein courant entre les surfaces-guides. D'autres, celles, qui restent fixées à la paroi, détruisent nos matériaux

comme nous allons l'expliquer maintenant. La figure 14 nous donne une photographie prise à l'aide du microscope, d'une partie d'une pale de la roue de la pompe endommagée pendant l'assèchement du Wieringermeer.



Fig. 14. Photographie agrandie d'une partie endommagée de la pale de la pompe de la station de pompage Lely.

Quelles sont les forces qui détruisent le matériel?

Dans le cas extrême où l'angle de contact est  $0^\circ$ , c'est à dire lorsque la bulle n'est en contact avec la paroi que par un point, le coup de marteau est dirigé vers la paroi et l'énergie capillaire  $A = 4\pi r_0^2 \gamma$  se décharge dans le point de contact.

Nous supposons qu'en réalité, les bulles ont la forme de demi-sphères comme celle représentée à la figure 13 et étudions plus au fond la distribution des pressions au moment de l'écroulement des bulles.

Imaginons nous d'abord que les bulles ne se contractent pas en un point mais que la surface a un creux demi-sphérique qui contient une sphère élastique, incompressible, sans masse et que la bulle demi-sphérique aboutit par toucher cette sphère comme le représente la figure 15.

Pour des raisons de symétrie et d'équilibre, la répartition des pressions ne peut pas être une autre que celle indiquée dans la figure.

Toutefois, il n'est pas question ici d'une charge statique, mais d'un coup de bélier de l'eau sur le métal, d'un choc entre deux corps élastiques.

Pour l'étudier, nous commenceront par calculer les pressions de contact entre deux barres de longueurs infinies, de section égale à l'unité, se heurtant de front par leur extrémité avec une vitesse relative  $v$ .

Désignons respectivement par  $\mu$  et  $E$  la masse spécifique et le coefficient d'élasticité des barres et par  $u$  la vitesse de propagation du son dans

celles-ci. Considérons l'instant où la pression  $p$  devient maximum, et soit  $w$  la vitesse du plan de séparation à cet instant. Considérons l'une des barres

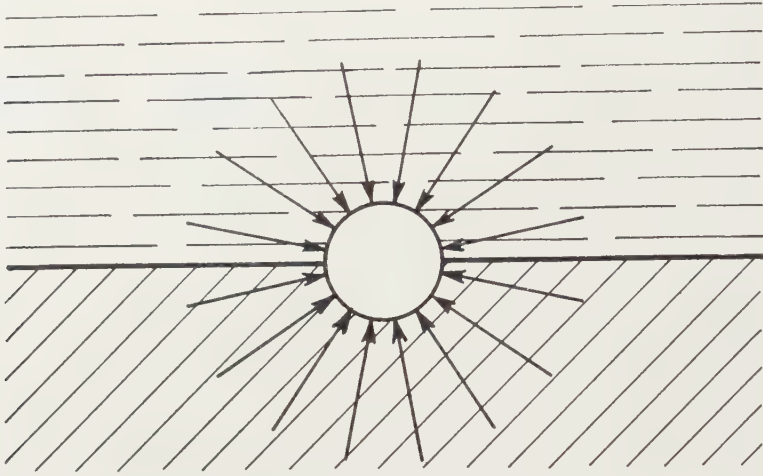


Fig. 15. Choc d'une bulle demi-sphérique se contractant sur une bille incompressible, sans masse, placée dans un creux de la surface d'une paroi.

et le front de l'onde sonore au repos, cette barre se déplaçant en sens contraire de la vitesse du son.

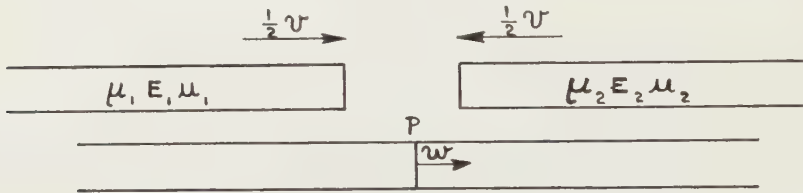


Fig. 16. Choc frontal de deux barres de matières différentes.

On sait que sous l'effet du choc une partie de la barre est comprimée sous la pression uniforme  $p$ , le front de l'onde sonore (limite entre la partie comprimée et la partie non-influencée encore par le choc), se déplace avec la vitesse du son.

On se rend compte facilement que

$$(\tfrac{1}{2} v - w) = \frac{p}{E_1} u_1$$

$$(\tfrac{1}{2} v + w) = \frac{p}{E_2} u_2$$

$$v = p \left( \frac{u_1}{E_1} + \frac{u_2}{E_2} \right) \quad p = \frac{E_1 \cdot E_2}{u_1 E_2 + u_2 E_1} \cdot \text{Or } u = \sqrt{\frac{E}{\mu}}.$$

donc

$$p = \frac{u_1 \mu_1 \times u_2 \mu_2}{u_1 \mu_1 + u_2 \mu_2} v \quad \text{ou } p = \frac{\sqrt{\mu_1 E_1} \times \sqrt{\mu_2 E_2}}{\sqrt{\mu_1 E_1} + \sqrt{\mu_2 E_2}} v.$$

On obtient les mêmes formules pour le choc transmis par un corps incompressible sans masse, posé entre les deux barres; et les formules restent aussi valables pour le cas représenté par la figure 15. Les deux dernières formules donnent donc la pression spécifique pour le cas où la bulle en contraction touche à la bille incompressible interposée,  $v$  étant calculé avec la formule indiquée à la page 332.

Quand il n'y a pas de bille interposée, quand la bulle demi-sphérique peut se contracter jusqu'à un point,  $v$  devient infini et les deux formules pour la pression donnent pour

$$v = \infty \quad p = \infty.$$

Aucun matériel ne résiste donc à l'écrasement des bulles, écrasement qui donne des pressions infiniment grandes.

#### 8. *Phénomène d'amorçage de la contraction des bulles et zone d'érosion.*

Mais, comment est amorcée la contraction des bulles? Revenons au cas du tuyau convergent-divergent.

Nous avons représenté sur la figure 17, le cas de cavitation de la première

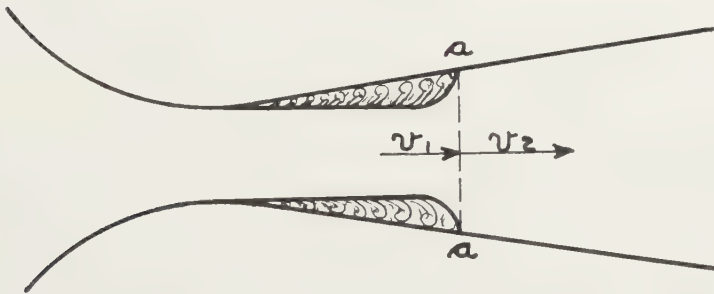


Fig. 17. Cavitation de la première catégorie, caractérisée par la disparition spontanée des bulles d'air le long d'une frontière limite qui oscille.

catégorie, qui est suffisante pour détruire nos matériaux de construction par érosion. Il y a un endroit sur la paroi où les bulles disparaissent<sup>1)</sup>.

Par suite de l'espace occupé par les bulles, jusqu'à la limite où elles disparaissent brusquement, les vitesses d'eau en amont de cette ligne sont considérablement augmentées.

Par contre, dès que la limite a été dépassée, la section d'eau redevient normale et le liquide subit de ce fait un sérieux ralentissement.

<sup>1)</sup> J. ACKERET. Experimentale und Theoretische Untersuchungen über Hohlraum-bildung im Wasser, p. 32, Stossvorgang in einem Kanal.



On peut calculer la surpression moyenne brusque due à ce ralentissement de  $v_1$  à  $v_2$  et on trouve

$$p_2 - p_1 = \frac{v_2 s}{g} (v_1 - v_2)^2 \quad ^1)$$

où  $s$  = poids spécifique du liquide.

Ce phénomène de choc (BORDA—BELLANGER), qui se produit également à la surface des pales des turbines de pompes et des hélices, est accompagné d'une dissipation d'énergie importante:  $\frac{(v_1 - v_2)^2}{2g} s$  par kg d'eau; celle-ci

est l'une des causes de baisse du rendement lorsque la cavitation s'accroît, mais n'explique pas les surpressions locales capables d'éroder les parois.

Mais ce ralentissement brusque du liquide, véritable choc global, comprime nos bulles, jusqu'à détruire l'équilibre entre la différence de la pression intérieure et extérieure et la tension superficielle.

Cette augmentation de pression, due au ralentissement, est même si importante qu'elle facilite la résorption de l'air, ce qui justifie l'hypothèse que nous avons faite en négligeant dans nos calculs la résistance à cette résorption.

Nous devons encore préciser pourquoi la zone de cavitation n'est pas limitée par une frontière bien définie. D'abord, dans nos machines hydrauliques, le régime n'est pas absolument stable par suite des grands remous toujours existants dans l'eau courante et par suite des variations de tension des moteurs d'entraînement ou génératrices. Ensuite les tourbillons engendrés dans la couche limite, étudiés par BURGERS et V. KÁRMÁN, produisent un va et vient de la frontière de disparition des bulles. Et ces bulles n'existent pas séparément.

Quand la cavitation destructive se manifeste, il faut se représenter une espèce de mousse se déplaçant dans la couche limite, contenant assez d'énergie de tension superficielle pour que la décharge brusque de cette énergie potentielle devienne dangereuse.

Lorsque les crevasses commencent à se former la destruction de la paroi s'accomplit ensuite rapidement. La mousse entre dans les fissures. Quand, dans son mouvement de va et vient, la limite de surpression ou ligne  $a-a$  balaye les fissures, les bulles d'air y sont d'abord comprimées par suite du ralentissement brusque de l'eau et leur énergie de capillarité s'y décharge.

Nous avons remarqué que le commencement de la cavitation est caractérisé par une augmentation du rendement de nos machines hydrauliques.

Avec le développement de nos laboratoires et l'application générale des

<sup>1)</sup> ANDRÉ TENOT: Etude théorique et expérimentale des pompes-hélices et essais de cavitation (laboratoire de l'Ecole nationale d'Arts et Métiers de Châlons sur Marne), p. 40, Turbines Hydrauliques. Livre II du même auteur.

On doit fortement recommander les publications de M. TENOT à celui qui veut se mettre au courant des questions de la cavitation.

essais sur modèle réduit on arrive souvent à adopter sans le savoir le régime de cavitation légère.

Or, avec les grands nombres de REYNOLDS c'est à dire pour les exécutions à grande échelle l'épaisseur de la couche limite est proportionnelle aux dimensions linéaires des organes mécaniques. Les dimensions des bulles, le temps de disparition, le chemin parcouru après le moment critique sont indépendants de l'échelle. Il s'ensuit que par unité de surface des organes, l'énergie superficielle mise en jeu augmente avec les dimensions linéaires et que pour les grandes machines hydrauliques ainsi que pour les hélices des bateaux les effets de cavitation peuvent être importants tandis qu'ils étaient imperceptibles pour les modèles.

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**Mathematics.** — *Verteilungsfunktionen.* Von J. G. VAN DER CORPUT.  
(Sechste Mitteilung).

(Communicated at the meeting of February 29, 1936).

*Beweis einer hinreichenden Bedingung.*

In der vierten Mitteilung (S. 21) <sup>1)</sup> habe ich Satz 20 formuliert, der eine hinreichende Bedingung liefert, damit eine vorgegebene Zahlenfolge so umgeordnet werden kann, dass die Menge der Verteilungsfunktionen der umgeordneten Menge eine vorgegebene Funktionenmenge sei. Die vorliegende Mitteilung enthält den Beweis dieses Satzes.

**Hilfssatz 11:** *Jeder Folge*

$$U: \quad u_1, u_2, \dots$$

kann eine positive Funktion  $g(\gamma)$  zugeordnet werden, mit der Eigenschaft dass für jedes ganze  $q > 0$  und für jede Funktion  $\chi(\gamma)$  mit Eigenschaft  $\mathfrak{G}(U)$  die Folge  $u_q, u_{q+1}, \dots$  eine Teilfolge  $V$  enthält, die für jedes  $\gamma$  und jedes ganze  $x > 0$  der Ungleichung

$$|V_\gamma(x) - x\chi(\gamma)| < 24\sqrt{x} + g(\gamma)$$

genügt.

*Beweis von Hilfssatz 11.*

*Erster Schritt:* Die Funktion

$$\psi(\gamma) = \chi(\gamma) - \sum_{\substack{q \text{ in } r(U) \\ q < \gamma}} r_q - \sum_{\substack{\sigma \text{ in } l(U) \\ \lambda \leq \gamma}} l_\lambda, \quad \dots \quad (97)$$

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<sup>1)</sup> Die vorigen Mitteilungen kommen vor in diesen Proceedings 38, 813–821, 1058–1066 (1935); 39, 10–19, 19–26, 149–153 (1936).

wo  $r_\rho = \chi(\rho+) - \chi(\rho)$  und  $l_\lambda = \chi(\lambda) - \chi(\lambda-)$  ist, ist stetig, monoton-nichtabnehmend,  $\geq 0$  und  $\leq 1$ . Für jedes Zahlpaar  $\eta$  und  $\zeta$  mit  $\eta \leq \zeta$  ist

$$\psi(\zeta) - \psi(\eta) \leq \chi(\zeta) - \chi(\eta). \quad . \quad . \quad . \quad . \quad . \quad (98)$$

*Beweis:* Für jedes Zahlpaar  $\eta$  und  $\zeta$  mit  $\eta \leq \zeta$  ist

$$\psi(\zeta) - \psi(\eta) = \chi(\zeta) - \chi(\eta) - \sum_{\substack{\rho \text{ in } r(U) \\ \eta \leq \rho < \zeta}} r_\rho - \sum_{\substack{\lambda \text{ in } l(U) \\ \eta < \lambda \leq \zeta}} l_\lambda, \quad . \quad . \quad (99)$$

sodass einerseits wegen  $r_\rho \geq 0$  und  $l_\lambda \geq 0$  Ungleichung (98) gilt, andererseits  $\psi(\zeta) - \psi(\eta) \geq 0$  ist. Hiermit ist die Monotonie von  $\psi(\gamma)$  bewiesen.

Aus (97) geht hervor

$$\lim_{\gamma \rightarrow -\infty} \psi(\gamma) = \lim_{\gamma \rightarrow -\infty} \chi(\gamma) \geq 0, \quad \text{also} \quad \psi(\gamma) \geq 0. \quad . \quad (100)$$

und

$$\psi(\gamma) \leq \chi(\gamma) \leq 1.$$

Die Funktion  $\chi(\gamma)$  besitzt die Eigenschaft  $\mathfrak{G}(U)$ . Diese Funktion, also wegen (97) auch  $\psi(\gamma)$ , ist somit ausserhalb  $r(U)$  nach rechts, ausserhalb  $l(U)$  nach links stetig. Aus (99) folgt: gehört  $\eta$  zu  $r(U)$ , so ist

$$\lim_{\substack{\zeta > \eta \\ \zeta \rightarrow \eta}} (\psi(\zeta) - \psi(\eta)) = \chi(\eta+) - \chi(\eta) - r_\eta = 0;$$

gehört  $\zeta$  zu  $l(U)$ , so ist

$$\lim_{\substack{\eta < \zeta \\ \eta \rightarrow \zeta}} (\psi(\zeta) - \psi(\eta)) = \chi(\zeta) - \chi(\zeta-) - l_\zeta = 0.$$

Folglich ist  $\psi(\gamma)$  in  $r(U)$  nach rechts, in  $l(U)$  nach links, also überall stetig.

Hiermit ist die Behauptung des ersten Schrittes bewiesen.

*Zweiter Schritt:* Wird

$$\lim_{\gamma \rightarrow -\infty} \psi(\gamma) = \lim_{\gamma \rightarrow -\infty} \chi(\gamma) = d_0 \quad (\text{vergl. (100)}); \quad . \quad . \quad (101)$$

$$1 - \lim_{\gamma \rightarrow \infty} \chi(\gamma) = d_1; \quad -d_0 + \lim_{\gamma \rightarrow \infty} \psi(\gamma) = d_2, \quad . \quad . \quad (102)$$

$$\psi_2(\gamma) = \frac{\psi(\gamma) - d_0}{d_2} \quad \text{falls } d_2 > 0 \quad . \quad . \quad . \quad (103)$$

$$= 0 \quad \text{falls } d_2 = 0$$

gesetzt, so besitzt, falls  $d_2 > 0$  ist,  $\psi_2(\gamma)$  die Eigenschaft  $\mathfrak{G}(U)$ .

*Beweis:* Nach dem ersten Schritt ist  $\psi_2(\gamma)$  stetig und monoton-nichtabnehmend. Aus der Definition folgt  $0 \leq \psi_2(\gamma) \leq 1$ .





beschränkt; und Häufungspunkt von  $U$  sich nicht ändern, wenn  $U$  durch  $u_q, u_{q+1}, \dots$  ersetzt wird).

Ich definiere nun folgendermassen  $v_x$  für  $x=1, 2, \dots$ . Die natürliche Zahl  $x$  kommt in einer und nur einer der  $k$  Mengen  $\mathfrak{D}^0, \mathfrak{D}^1, \mathfrak{D}^2, \mathfrak{R}^e, \mathfrak{L}^\lambda$  vor. Kommt  $x$  in  $\mathfrak{D}^\kappa$  ( $0 \leq \kappa \leq 2$ ) vor, so sei  $v_x$  die  $\mathfrak{D}_\kappa^{\text{te}}$  in  $D^\kappa$  auftretende Zahl; kommt  $x$  in  $\mathfrak{R}^e$  vor, so sei  $v_x$  die  $\mathfrak{R}_e^{\text{te}}$  in  $R^e$  auftretende Zahl und kommt schliesslich  $x$  in  $\mathfrak{L}^\lambda$  vor, so sei  $v_x$  die  $\mathfrak{L}_\lambda^{\text{te}}$  in  $L^\lambda$  auftretende Zahl. So ist die Folge

$$V: \quad v_1, v_2, \dots$$

testgelegt.

Die Funktion  $g(\gamma)$  werde definiert wie folgt: für jeden Häufungspunkt von  $U$  sei  $g(\gamma) = 3|\gamma|$ ; sonst sei

$$g(\gamma) = 3|\gamma| + \frac{3}{\gamma - \alpha} + \frac{3}{\beta - \gamma}; \quad . \quad . \quad . \quad . \quad . \quad (109)$$

hierin bezeichnet  $(\alpha, \beta)$  das grösste  $\gamma$  enthaltende Intervall, das in seinem Innern keinen Häufungspunkt von  $U$  enthält.

*Vierter Schritt:* Abschluss des Beweises. Die Folge  $u_q, u_{q+1}, \dots$  ist in  $k+1$  Teilmengen  $D^0, D^1, D^2, R^e, L^\lambda, Z$  zerlegt.  $V$  ist aus zu  $D^0, D^1, D^2, R^e, L^\lambda$  gehörigen Zahlen aufgebaut, ist somit eine Teilfolge von  $u_q, u_{q+1}, \dots$ . Aus der im vorigen Schritt gegebenen Definition von  $V$  folgt für jedes  $\gamma$  und jedes ganze  $x > 0$

$$V_\gamma(x) = \sum_{\kappa=0}^2 D_\gamma^\kappa(\mathfrak{D}_\kappa) + \sum_{\varrho \text{ in } \mathfrak{r}(U)} R_\gamma^\varrho(\mathfrak{R}_\varrho) + \sum_{\lambda \text{ in } \mathfrak{l}(U)} L_\gamma^\lambda(\mathfrak{L}_\lambda);$$

hierin ist, falls  $d_1^0, d_2^0, \dots$  die Folge  $D^0$  bezeichnet,  $D_\gamma^0(t)$  die Anzahl der Zahlen  $d_\xi^0 < \gamma$  mit  $\xi \leq t$ ; analog  $D_\gamma^1(t)$ ,  $D_\gamma^2(t)$ ,  $R_\gamma^\varrho(t)$ , und  $L_\gamma^\lambda(t)$ .

Durch Anwendung der 5 im vorigen Hilfssatz genannten Eigenschaften, bzw. mit  $x = \mathfrak{D}_0, \mathfrak{D}_1, \mathfrak{D}_2, \mathfrak{R}_e$  und  $\mathfrak{L}_\lambda$  angewendet, liefert die obige für  $V_\gamma(x)$  gefundene Beziehung die Ungleichung

$$\left| V_\gamma(x) - \mathfrak{D}_0 - \mathfrak{D}_2 \psi_2(\gamma) - \sum_{\substack{\varrho \text{ in } \mathfrak{r}(U) \\ \varrho < \gamma}} \mathfrak{R}_\varrho - \sum_{\substack{\lambda \text{ in } \mathfrak{l}(U) \\ \lambda \leq \gamma}} \mathfrak{L}_\lambda \right| \left( \right. \\ \left. \leq \frac{1}{2}|\gamma| + \frac{1}{2}|\gamma| + 2 + 2 \log x + \sum' \frac{1}{\gamma - \varrho} + \sum'' \frac{1}{\lambda - \gamma}; \right) \quad (110)$$

hierin wird die Summe  $\sum'$  erstreckt über die etwigen in  $\mathfrak{r}(U)$  vorkommenden  $\varrho$  mit  $\varrho < \gamma < P_\varrho$ , und die Summe  $\sum''$  über die etwigen in  $\mathfrak{l}(U)$  vorkommenden  $\lambda$  mit  $A_\lambda < \gamma < \lambda$ .

Aus den im vorigen Hilfssatz für  $P_\varrho$  und  $A_\lambda$  gegebenen Definitionen geht hervor, dass jede der zwei Summen  $\sum'$  und  $\sum''$  aus höchstens einem Gliede besteht, und dieses Glied ist wegen (109) höchstens  $\frac{1}{3}g(\gamma)$ , sodass

die rechte Seite von (110) wegen  $|\gamma| \leq \frac{1}{3}g(\gamma)$  und  $1 + \log x < 2\sqrt{x}$  kleiner ist als  $4\sqrt{x} + g(\gamma)$ . Aus (105) und (108) folgt dann

$$|V_\gamma(x) - d_0 x - d_2 x \psi_2(\gamma) - x \sum_{\substack{\varrho \text{ in } r(U) \\ \varrho < \gamma}} r_\varrho - x \sum_{\substack{\lambda \text{ in } l(U) \\ \lambda \leq \gamma}} l_\lambda| \\ < 4\sqrt{x} + g(\gamma) + 5\sqrt{x} + 5\sqrt{x} + 10\sqrt{x} = 24\sqrt{x} + g(\gamma).$$

Hieraus geht die Behauptung hervor; denn aus (97) folgt

$$d_0 + d_2 \psi_2(\gamma) + \sum_{\substack{\varrho \text{ in } r(U) \\ \varrho < \gamma}} r_\varrho + \sum_{\substack{\lambda \text{ in } l(U) \\ \lambda \leq \gamma}} l_\lambda = d_0 + d_2 \psi_2(\gamma) + \chi(\gamma) - \psi(\gamma). \quad (111)$$

$= \chi(\gamma)$  falls (103) gilt,

und sonst ist  $\psi_2(\gamma)$  identisch gleich Null und  $d_2 = 0$ , also wegen (101) und (102)  $\psi(\gamma)$  identisch gleich  $d_0$ , sodass auch dann Ausdruck (111) gleich  $\chi(\gamma)$  ist.

### Beweis von Satz 20.

Nach dem vorigen Hilfssatz, mit  $q = q_1 = 1$  angewendet, enthält  $U$  eine Teilfolge

$$V^1: \quad v_1^{(1)}, v_2^{(1)}, \dots \text{ mit } |V_\gamma^1(x) - x \varphi_1(\gamma)| < 24\sqrt{x} + g(\gamma),$$

gültig für jedes  $\gamma$  und jedes ganze  $x \geq 1$ ; hierin ist  $V_\gamma^1(x)$  die Anzahl der Zahlen  $v_\xi^{(1)} < \gamma$  mit  $\xi \leq x$  (analog  $V_\gamma^n(x)$  nachher).

Ich wähle die natürliche Zahl  $q_2$  so gross, dass  $v_1^{(1)}$  im System  $u_1, u_2, \dots, u_{q_2-1}$  vorkommt. Wiederum nach dem vorigen Hilfssatz, aber jetzt mit  $q = q_2$  angewendet, enthält die Folge  $u_{q_2}, u_{q_2+1}, \dots$  eine Teilfolge

$$V^2: \quad v_1^{(2)}, v_2^{(2)}, \dots \text{ mit } |V_\gamma^2(x) - x \varphi_2(\gamma)| < 24\sqrt{x} + g(\gamma).$$

Ich wähle nun die natürliche Zahl  $q_3$  so gross, dass  $(v_1^{(1)}, v_1^{(2)}, v_2^{(2)})$  ein Teilsystem von  $(u_1, \dots, u_{q_3-1})$  ist und ich wende wiederum den vorigen Hilfssatz an. So weitergehend finde ich natürliche Zahlen  $q_1, q_2, \dots$  und Folgen

$$V^n: \quad v_1^{(n)}, v_2^{(n)}, \dots \quad (n \geq 1)$$

mit folgenden Eigenschaften:

Ist  $n \geq 2$ , so bilden die Zahlen  $v_\tau^{(v)} (v = 1, \dots, n-1; \tau = 1, \dots, v!)$  ein Teilsystem von  $(u_1, \dots, u_{q_n-1})$ ; für jedes  $n \geq 1$  ist  $V^n$  eine Teilfolge von  $u_{q_n}, u_{q_n+1}, \dots$ , und für jedes  $n \geq 1$ , jedes  $\gamma$  und jedes ganze  $x > 0$  gilt die Ungleichung

$$|V_\gamma^n(x) - x \varphi_n(\gamma)| < 24\sqrt{x} + g(\gamma). \quad (112)$$

Die Folge

$$T: \quad v_1^{(1)}, v_1^{(2)}, v_2^{(2)}, v_1^{(3)}, \dots, v_6^{(3)}, \dots, v_1^{(n)}, \dots, v_n^{(n)}, \dots$$



**Mathematics. — Ueber einige VINOGRADOFFsche Methoden.** Von  
J. G. VAN DER CORPUT. (Erste Mitteilung).

(Communicated at the meeting of February 29, 1936).

Herr I. M. VINOGRADOFF hat der Zahlentheorie sehr vernünftige und überaus fruchtbare Methoden geschenkt. Der Entdecker veröffentlicht seine Beweise fast nur in Russisch und dabei noch so kurz gefasst, dass die Lektüre nicht leicht ist. Ich beabsichtige in diesen Noten einige seiner Methoden zu behandeln, zu verallgemeinern und etwas zu verschärfen. Um diese Mitteilungen zu verstehen, ist es nicht nötig, die VINOGRADOFFschen Arbeiten zu kennen.

In dieser ersten Mitteilung geht es zunächst um die Frage, wie scharf eine beliebig vorgegebene reelle Zahl  $\alpha$  durch einen Bruch  $\frac{z}{u^k}$ , dessen Nenner gleich der  $k^{\text{ten}}$  Potenz einer natürlichen Zahl  $u$  ist, approximiert werden kann; hierin ist  $k$  eine vorgegebene natürliche Zahl. Eine Antwort auf diese Frage bekommt der Leser in den folgenden zwei VINOGRADOFFschen Sätzen<sup>1)</sup>.

**Satz 1:** Ist  $k \geq 1$  ganz,  $\varepsilon = 2^k$  und  $\varepsilon > 0$ , so gehören zu jedem reellen  $\alpha$  unendlich viele Brüche  $\frac{z}{u^k}$  mit

$$\left| \alpha - \frac{z}{u^k} \right| < u^{-k - \frac{2k}{k+2} + \varepsilon}.$$

**Satz 2:** Ist  $k \geq 10$  ganz, so gehören zu jedem reellen  $\alpha$  unendlich viele Brüche  $\frac{z}{u^k}$  mit

$$\left| \alpha - \frac{z}{u^k} \right| < u^{-k - \frac{1}{15k^2 \log 10k}}.$$

Man beachte, dass Satz 2 für grosses  $k$  viel schärfer als Satz 1 ist, weil dann  $\frac{1}{2k} (k+2)$  viel grösser als  $15k^2 \log 10k$  wird.

In dieser Mitteilung werde ich u.a. beweisen:

<sup>1)</sup> Satz 1 kommt vor in: Analytischer Beweis des Satzes über die Verteilung der Bruchteile eines ganzen Polynoms, Bull. Acad. Sci. URSS (6), 21 (1927) S. 567—578 (Russisch). Satz 2 in: Sur l'approximation au moyen des fractions rationnelles, dont les dénominateurs sont des puissances de nombres entiers. C. R. Acad. Sci. URSS 1935II, S. 1—5 (Russisch mit französischem Auszug).





Dann gehört zu jedem dieser Brüche  $\frac{p}{q}$  mit hinreichend grossem Nenner und zu jedem reellen  $\beta$  mindestens ein System ganzer Zahlen  $x, y, z$  mit

$$0 < a f(x) g(y) - \beta - z < x^{-\xi} y^{-\eta}, \dots \dots \dots (3)$$

$$Y \leq y < 2Y; \quad 1 \leq x < 2Y^{\frac{t-1-\eta}{n+\xi}} \quad \text{und} \quad \liminf_{q \rightarrow \infty} \frac{\log x}{\log q} > 0 \dots \dots (4)$$

Ich behaupte noch mehr: bei geeignet nur von  $n, t, \xi$  und  $\eta$  abhängigem positivem  $\delta$  gehört sogar zu jedem der Brüche  $\frac{p}{q}$  mit hinreichend grossem Nenner und zu jedem reellen  $\beta$  mindestens ein System ganzer Zahlen  $x, y, z$  mit (4) und

$$0 < a f(x) g(y) - \beta - z < x^{-\xi-\delta} y^{-\eta-\delta} \dots \dots \dots (5)$$

Die zweite Mitteilung ist dem Beweis dieses Satzes gewidmet; in der vorliegenden ersten Mitteilung behandle ich einige Anwendungen. Aus Satz 4 geht unmittelbar hervor:

**Satz 5:** Ist Voraussetzung A erfüllt und ist

$$\limsup_{x \rightarrow \infty} \frac{\log g(x)}{\log x} \leq t, \dots \dots \dots (6)$$

so hat (3) für jedes reelle irrationale  $\alpha$  und jedes reelle  $\beta$  unendlich viele ganzzahlige Lösungen  $x, y, z$ , wobei  $x$  und  $y$  positiv sind.

Wird  $\xi$  durch (1) festgelegt und ist  $k \geq 2$  ganz, so sind Voraussetzung A und (6) mit

$$n = t = k; \quad \xi = \eta = \frac{1}{\zeta}; \quad f(x) = g(x) = x^k \dots \dots \dots (7)$$

erfüllt, sodass die Ungleichung

$$0 < a (xy)^k - \beta - z < (xy)^{\frac{1}{\zeta}}$$

für jedes reelle irrationale  $\alpha$  und jedes reelle  $\beta$  unendlich viele ganzzahlige Lösungen  $x, y, z$  mit positiven  $x$  und  $y$  besitzt; Satz 3 (der für rationales  $\alpha$  evident ist) ist also nur ein Spezialfall von Satz 5.

Satz 5 liefert aber noch viel mehr. Setzt man z.B.

$$f(x) = g(x) = p_x^k \qquad (k \geq 2 \text{ ganz}),$$

wo  $p_x$  die  $x^{\text{te}}$  Primzahl bezeichnet, und wird  $\zeta$  wiederum durch (1) definiert, so sind die Voraussetzung A und die Bedingung (6) mit

$n = t = k$  und  $\xi = \eta = \frac{1}{\zeta}$  erfüllt. Folglich gehören zu jedem irrationalen  $\alpha$  unendlich viele Systeme ganzzahliger  $p, p', z$  mit

$$0 < \alpha - \frac{z}{(pp')^k} < (pp')^{-k - \frac{1}{\zeta}},$$

wobei  $p$  und  $p'$  sogar Primzahlen sind.

Die regelmässige Kettenbruchentwicklung der irrationalen Zahl  $\alpha$

$$\alpha = b_0 + \frac{1}{b_1 + \frac{1}{\ddots}}$$

liefert die Näherungsbrüche

$$\frac{p_m}{q_m} = b_0 + \frac{1}{b_1 + \frac{1}{\ddots + \frac{1}{b_m}}} \quad (m \geq 0)$$

von  $\alpha$ , die im folgenden Satz auftreten.

**Satz 6:** Gilt für die Näherungsbrüche der irrationalen Zahl  $\alpha$  die Beziehung

$$\limsup_{m \rightarrow \infty} \frac{\log q_m}{\log q_{m-1}} \leq \frac{t}{t-1}, \quad \dots \quad (8)$$

so darf in Satz 5 die Voraussetzung (6) durch die weniger forderende Ungleichung

$$\liminf_{x \rightarrow \infty} \frac{\log g(x)}{\log x} \leq t$$

ersetzt werden.

**Beweis:** Wegen der letzten Ungleichung gibt es eine Folge unbeschränkt wachsender natürlicher Zahlen  $Y$  mit (2). Bezeichnet  $\frac{p}{q} = \frac{p_m}{q_m}$  den ersten Näherungsbruch von  $\alpha$  mit  $q_m \geq Y^{t-1}$ , so ist

$$\limsup_{q \rightarrow \infty} \frac{\log Y}{\log q} \leq \frac{1}{t-1}.$$

Für hinreichend grosses  $q$  ist  $Y^{t-1} > q_{m-1}$ , also wegen (8)

$$\liminf_{q \rightarrow \infty} \frac{\log Y}{\log q} \leq \frac{1}{t-1} \quad \liminf_{m \rightarrow \infty} \frac{\log q_{m-1}}{\log q_m} \geq \frac{1}{t}.$$

Folglich sind die Voraussetzungen von Satz 4 erfüllt, sodass die Behauptung von Satz 4, also von Satz 5 gilt.

**Satz 7:** Ist Voraussetzung A mit  $\xi=0$  und  $\frac{1}{\eta}=8+\frac{16}{3}n \log 8(t-1)$  erfüllt, gilt (6) und genügen die Näherungsbrüche der irrationalen Zahl  $\alpha$  der Beziehung (8), so gehört zu jedem hinreichend grossen  $L$  und zu jedem reellen  $\beta$  mindestens ein System ganzer Zahlen  $x, y, z$  mit

$$0 < \alpha f(x) g(y) - \beta - z < \frac{1}{L}; \quad 1 \leq x < L^{\frac{t-1-\eta}{n\eta}} \text{ und } 1 \leq y < L^{\frac{1}{\eta}}.$$

**Beweis:** Jeder Zahl  $L \geq 2^\eta$  und  $\geq 2^{\frac{n\eta}{t-1-\eta}}$  ordne ich die grösste natürliche Zahl  $Y$  mit

$$2Y \leq L^{\frac{1}{\eta}} \text{ und } 2Y^{\frac{t-1-\eta}{n}} \leq L^{\frac{t-1-\eta}{n\eta}}$$

zu. Bezeichnet dann wiederum  $\frac{p}{q} = \frac{p_m}{q_m}$  den ersten Näherungsbruch von  $\alpha$  mit  $q_m \leq Y^{t-1}$ , so zeigt man genau wie beim Beweis des vorigen Satzes, dass die Voraussetzungen von Satz 4 erfüllt sind. Nach der zweiten Behauptung von Satz 4 besitzt die Ungleichung

$$0 < \alpha f(x) g(y) - \beta - z < y^{-\eta-\delta},$$

wo  $\delta$  eine geeignet gewählte, nur von  $n$  und  $t$  abhängige positive Zahl bezeichnet, eine ganzzahlige Lösung  $x, y, z$  mit

$$1 \leq x < 2Y^{\frac{t-1-\eta}{n}} \leq L^{\frac{t-1-\eta}{n\eta}}$$

und

$$1 \leq Y \leq y < 2Y < L^{\frac{1}{\eta}}.$$

Aus der Definition von  $Y$  folgt  $Y^{\eta+\delta} > L$  für hinreichend grosses  $L$ , also  $y^{-\eta-\delta} \leq Y^{-\eta-\delta} < \frac{1}{L}$ . Hiermit ist Satz 7 bewiesen.

Der Spezialfall dieses Satzes mit  $n=t=k$ ,  $f(x)=g(x)=x^k$  und  $\beta=0$  liefert

**Satz 8:** Ist  $k \geq 2$  ganz,  $\frac{1}{\eta} = 8 + \frac{16}{3}k \log 8(k-1)$  und erfüllen die Näherungsbrüche  $\frac{p_m}{q_m}$  der irrationalen Zahl  $\alpha$  die Beziehung

$$\limsup_{m \rightarrow \infty} \frac{\log q_m}{\log q_{m-1}} \leq \frac{k}{k-1}, \quad \dots \dots \dots (9)$$



so gehört zu jedem hinreichend grossen  $L$  mindestens ein Bruch  $\frac{z}{u^k}$  mit

$$\left| \alpha - \frac{z}{u^k} \right| < \frac{1}{L u^k} \text{ und } 1 \leq u < L^{\frac{2k-1-\eta}{k\eta}}.$$

Wird die Bedingung (9) weggelassen, so finde ich ein viel unschärferes Resultat, nämlich:

**Satz 9:** Ist  $k \geq 2$  ganz, so gehört zu jedem reellen  $\alpha$  und zu jedem hinreichend grossen  $L$  wenigstens ein Bruch  $\frac{z}{u^k}$  mit

$$\left| \alpha - \frac{z}{u^k} \right| < \frac{1}{L u^k} \text{ und } 1 \leq u < L^{\frac{32}{3} k^2 \log 8 (k-1)}.$$

**Beweis:** Ich darf  $\alpha$  irrational voraussetzen, da die Behauptung sonst evident ist. Ich unterscheide verschiedene Fälle.

1. Es gebe einen Näherungsbruch  $\frac{p}{q}$  von  $\alpha$  mit

$$q^{\frac{1}{k}} \leq L^{\frac{1}{\eta}} \leq q^{\frac{1}{k-1}}.$$

Ich wende Satz 4 mit  $n=t=k$ ;  $f(x)=g(x)=x^k$ ;  $\beta=0$ ;  $\xi=0$  und  $\eta^{-1}=8+\frac{16}{3}k \log 8 (k-1)$  an, wobei  $Y$  die grösste ganze Zahl mit

$$4 Y^{\frac{2k-1-\eta}{k}} \leq L^{\frac{2k-1-\eta}{k\eta}}$$

bezeichnet. Nach Satz 4 gibt es dann eine nur von  $k$  abhängige positive Zahl  $\delta$  mit folgender Eigenschaft: ist  $L$  hinreichend gross, so gibt es einen Bruch  $\frac{z}{u^k}$  mit

$$\left| \alpha - \frac{z}{u^k} \right| < \frac{1}{u^k Y^{\eta+\delta}} \text{ und } 1 \leq u < L^{\frac{2k-1-\eta}{k\eta}}.$$

Aus der Definition von  $Y$  folgt, dass  $Y^{\eta+\delta}$  für hinreichend grosses  $L$  grösser als  $L$  ist, sodass die Behauptung wegen

$$\frac{2k-1-\eta}{k\eta} < \frac{2}{\eta} = 16 + \frac{32}{3} k \log 8 (k-1) < \frac{32}{3} k^2 \log 8 (k-1)$$

gilt.

2. Tritt der unter 1. genannte Fall nicht auf, so gibt es bei hinreichend

grossen  $L$  zwei konsequente Näherungsbrüche  $\frac{P}{Q}$  und  $\frac{p}{q}$  von  $\alpha$  mit  $Q < q$  und

$$Q^{k-1} < L^{\frac{1}{\eta}} < q^k.$$

Ist  $q \geq L Q^{k-1}$ , so ist

$$\left| \alpha - \frac{P}{Q} \right| < \frac{1}{Qq} < \frac{1}{L Q^k} \text{ und } Q < L^{\frac{k-1}{\eta}},$$

sodass wegen  $\frac{k-1}{\eta} < \frac{32}{3} k^2 \log 8 (k-1)$  die Behauptung mit  $u=Q$  und  $z=P Q^{k-1}$  gilt. Ich darf also  $q < L Q^{k-1}$  annehmen, und ich wende jetzt wiederum Satz 4 mit  $\xi=0$  und  $\eta^{-1}=8 + \frac{16}{3} k \log 8 (k-1)$  an, wobei  $Y$  die grösste ganze Zahl mit

$$4 Y^{\frac{2k-1-\eta}{k}} \leq q^{\frac{2k-1-\eta}{k^2}}$$

bezeichnet. Ich bekomme so eine nur von  $k$  abhängige positive Zahl  $\delta$  mit folgender Eigenschaft: ist  $L$  hinreichend gross, so gibt es einen Bruch  $\frac{z}{u^k}$  mit

$$\left| \alpha - \frac{z}{u^k} \right| < \frac{1}{u^k Y^{\eta+\delta}} \text{ und } 1 \leq u \leq 4 Y^{\frac{2k-1-\eta}{k}}.$$

Für hinreichend grosses  $L$  ist  $Y^{\eta+\delta}$  grösser als  $q^{\frac{\eta}{k}} > L$  und man hat

$$u \leq q^{\frac{2k-1-\eta}{k^2}} < (L Q^{k-1})^{\frac{2k-1-\eta}{k^2}} < L^{\left(1 + \frac{(k-1)^2}{\eta}\right) \cdot \frac{2k-1-\eta}{k^2}}.$$

Der letzte Exponent ist wegen  $\eta < 1$  und  $\frac{1}{\eta} < \frac{8}{3} (3+2k) \log 8 (k-1)$  kleiner als

$$\begin{aligned} \left( \frac{1}{\eta} + \frac{k^2-2k+1}{\eta} \right) \frac{2k-1}{k^2} &< \frac{8}{3} \cdot \frac{(k^2-2k+2)(2k-1)(3+2k)}{k^2} \log 8 (k-1) \\ &< \frac{32}{3} \frac{(k^2-2k+2)(k+1)}{k} \log 8 (k-1) \\ &< \frac{32}{3} k^2 \log 8 (k-1), \end{aligned}$$

womit Satz 9 bewiesen ist.

Für  $k \geq 10$  hat Herr VINOGRADOFF das entsprechende Resultat gegeben, aber mit dem etwas grösseren Exponenten  $15 k^2 \log 10 k$  statt  $\frac{32}{3} k^2 \log 8 (k-1)$ . Es ist klar, dass diese VINOGRADOFFSche Behauptung Satz 2 als Spezialfall enthält.

**Chemistry.** — *Der Einfluss mechanischer Deformation auf die Umwandlungsgeschwindigkeit polymorpher Metalle II. Der Einfluss metallischer Beimengungen.* Von ERNST COHEN und A. K. W. A. VAN LIESHOUT.

(Communicated at the meeting of February 29, 1936).

### *Einleitung.*

Nachdem wir in unserer ersten Arbeit<sup>1)</sup> den Einfluss mechanischer Deformation auf die Umwandlungsgeschwindigkeit eines *reinen* polymorphen Metalls (Zinn) studiert hatten, lag es auf der Hand nunmehr diesen Einfluss zu untersuchen, falls es sich um ein Metall handelte, welches geringe metallische Beimengungen enthielt. Diesem Problem kommt eine um so grössere Bedeutung zu, als in der Technik ja fast immer mechanisch deformierte Metalle zur Verwendung kommen, welche kleinere bzw. grössere Mengen von Fremdmetallen enthalten.

Bereits gelegentlich der ersten Studien über die Umwandlung von weissem in graues Zinn legte J. FRITZSCHE<sup>2)</sup> sich die Frage vor, ob sich ein solcher Einfluss nachweisen liess. Da seine Erfahrungen sich aber nicht mit denjenigen der Technik deckten, schloss er den betreffenden Passus seiner Mitteilung mit den Worten: „Auch hier werden weitere Versuche mehr Aufklärung bringen“.

Auch P. FARUP<sup>3)</sup>, sowie G. TAMMANN und K. L. DREYER<sup>4)</sup> und in jüngster Zeit C. W. MASON und W. D. FORGENG<sup>5)</sup> haben sich mit dieser Frage befasst; da diesen Autoren, deren Arbeiten wir später ausführlich zu besprechen beabsichtigen, der enorme Einfluss der thermischen und mechanischen Vorgeschichte auf die Umwandlungsgeschwindigkeit des Zinns, welcher von uns in letzter Zeit festgestellt wurde, selbstverständlich nicht bekannt sein konnte, haben wir das Problem unter Zugrundelegung unserer jüngsten Erfahrungen aufs neue studiert. Es galt somit die Frage zu beantworten: welchen Einfluss übt der Zusatz von Beimengungen fremder Metalle auf die Umwandlungsgeschwindigkeit von weissem Zinn bekannter mechanischer und thermischer Vorgeschichte.

### *Materialien und Versuchstechnik.*

1. Das von uns verwendete Zinn entstammte einem Block Banka Zinn (Sn 99.950 %; Sb 0.007 %; As nil; Pb Spur; Bi nil; Cu 0.018 %;

<sup>1)</sup> Proc. Royal Acad. Amsterdam, **38**, 377 (1935).

<sup>2)</sup> Mém. l'acad. imp. sci. St. Pétersbourg (7) **15**, N<sup>o</sup>. 5 (1870).

<sup>3)</sup> Teknisk Ugeblad **55**, 29. Mai (1908); Tids. Kemi, Farm. terapi N<sup>o</sup>. 11 und 12 (1908).

<sup>4)</sup> Z. anorg. allgem. Chem. **199**, 97 (1931).

<sup>5)</sup> Metals and Alloys, Page 87, April 1935.

Fe 0.045 %; Ag nil; S Spur). Die Metalle *Pb*, *Sb*, *Bi*, *Cd* und *Zn* waren die reinsten KAHLBAUMprodukte; das *Al* in Drahtform war Aluminium metallic. von MERCK, während unser *Ag* reinstes Münzsilber war, von der Reichsmünze hierselbst bezogen<sup>1)</sup>).

2. Die Zinnlegierungen stellten wir uns folgendermassen her: Gewogene Mengen der betreffenden Metalle schmolzen wir in ein Pyrexglasrohr in vacuo ein, welches sodann erhitzt wurde. Nachdem der Inhalt sich verflüssigt hatte, schüttelten wir das Rohr kräftig und liessen durch Umdrehen desselben die Schmelze in den unteren Teil fliessen. Nachdem das Ganze an der Luft auf Zimmertemperatur gekühlt war, entfernten wir das Glasrohr. Der so gebildete Metallstab hatte einen Durchmesser von 11 mm. Nachdem die Oberfläche desselben mittels einer Feile gereinigt war, walzten wir die Stäbe von 11 auf 4 mm, wobei sowohl das Metall wie die Walze in der früher beschriebenen Weise<sup>2)</sup> auf  $-80^{\circ}\text{C}$ . gehalten wurde. Den so gebildeten Draht zerschnitten wir in Stücke von je 7 cm Länge und schmolzen dieselben in Glasröhrchen von 7 mm innerem Durchmesser ein. Sodann brachten wir diese in ein Bad<sup>2)</sup> von  $-50^{\circ}\text{C}$ . und beobachteten den Gang der Umwandlung nach je 24 Std.

3. Es stellte sich dabei die überraschende Tatsache heraus, dass manche der zugesetzten Metalle die Umwandlungsgeschwindigkeit des mechanisch deformierten Zinns verlangsamten, andere dagegen dieselbe beschleunigten. Dementsprechend geben wir unsere Resultate in zwei Abschnitten.

#### A. Metalle, welche die Umwandlungsgeschwindigkeit des mechanisch deformierten Zinns verlangsamten.

4. Unsere Tabelle 1 enthält die Versuchsergebnisse. In der Kolumne mit der Ueberschrift „Zeit“ sind die Zeiten (in 24 Std. als Einheit) ver-

<sup>1)</sup> Ueber die „KAHLBAUM“-Präparate teilte uns die Firma SCHERING-KAHLBAUM A. G. — Berlin freundlichst Folgendes mit:

*Blei in Stangen zur Analyse:* Untersuchung von 50 g ergab:

*Ag* ca. 3—8 g pro Tonne; *Sb* geringe Spuren; *Bi* nicht erkennbar; *As* nach MARSH bei der Verwendung von 10 g Metall sehr häufig abwesend. *Cu-Sn-Cd-Ni-Zn* nicht erkennbar. *Fe* geringe Spuren und auch weniger. Auf *P*, *S*, *Se* und *Te* ist nicht geprüft worden. Diese Stoffe dürften aber, wenn überhaupt, nur in ganz geringen Spuren in dem Präparat enthalten sein.

*Antimon:* Schmelzpunkt  $630.51-0.03^{\circ}$ .

$\text{Al}_2\text{O}_3$   $4 \cdot 10^{-5}$ ;  $\text{SiO}_2$   $3 \cdot 10^{-5}$ ; *As*  $2 \cdot 10^{-4}$ ; *Pb*  $2 \cdot 10^{-5}$ ; *Zn*  $3 \cdot 10^{-6}$ ; *Fe*  $3 \cdot 10^{-6}$ .

*Cadmium:* 99.9 %, höchstens Hauch Eisen, so gut wie bleifrei, nicht völlig zinkfrei, frei von Kupfer, Nickel, Thallium und Mangan.

*Zink:* in 20 g kein Arsen, höchstens 0.05 % Fremdmetalle (*Blei*, *Cadmium*), höchstens 0.001 % *Mn*, höchstens 0.00025 % *Fe*, zuweilen nicht völlig frei von *S* und *P* (nach MERCK geprüft) 99.95 %.

<sup>2)</sup> Proc. Royal Acad. Amsterdam, 38, 377 (1935), Speziell § 8.



TABELLE 1.  
Temperatur — 50° C.

Zeit	10/0 Bi	10/0 Pb	10/0 Sb	10/0 Cd	10/0 Ag	500/0 Pb	Banka
1	0	0	0	0	0	0	0
2	0	0	0	0	0	0	0
3	0	0	0	0	0	0	0
4	0	0	0	0	0	0	0
5	0	0	0	0	0	0	3
7	0	0	0	0	1	0	
8	0	0	0	0	3	0	
18	0	0	0	3		0	
43	0	0	0			0	

zeichnet, während welcher die Drähte auf —50° C. gehalten waren. Es wurde stets, falls nicht anders bemerkt, mit drei Drähten derselben Legierung bzw. des Banka-Zinns experimentiert.

Die Zahlen in den anderen Kolonnen bezeichnen die Anzahl der Drähte, bei welchen nach den betreffenden Zeiten das Eintreten der Zinnpest sichtbar wurde.

Die Zahlen der Kolonne, welche mit „Banka“ überschrieben ist, beziehen sich auf Banka-Zinn von der oben (§ 1) genannten Zusammensetzung, welches *dieselbe mechanische (thermische) Vorgeschichte hatte als die untersuchten Legierungen*.

Der Tabelle 1 lässt sich entnehmen, dass während das Banka-Zinn bereits nach 5 Tagen von der Zinnpest befallen ist, die Legierungen, welche ein Prozent *Bi*, *Pb*, bzw. *Sb* enthalten, selbst nach 43 Tagen noch keine Spur davon aufweisen. Der Zusatz von 1 % *Cd* bewirkt, dass erst nach 18 Tagen, der von 1 % *Ag*, dass erst nach 8 Tagen die Umwandlung eintritt. Bei den 50 % *Pb* enthaltenden Drähten (Legierung, welche zum Löten verwendet wird) ist die Zinnpest nach 43 Tagen noch nicht sichtbar.

5. Im Anschluss an die Untersuchung von MASON und FORGENG, welche die Zeit, während welcher sie ihre Versuche fortsetzten, nicht angeben und die mechanische und thermische Vorgeschichte ihres Materials nicht definieren, zogen wir *Bi*-Legierungen in den Kreis unserer Untersuchung, welche 0.1; 0.01 bzw. 0.001 % *Bi* enthielten und der in § 2 beschriebenen mechanischen (thermischen) Vorbehandlung unterworfen gewesen waren.

Unsere Tabelle 2 enthält die diesbezüglichen Ergebnisse, welche die stark verlangsamende Wirkung auch sehr geringer Spuren *Bi* beleuchtet.

TABELLE 2.  
Temperatur  $-50^{\circ}$  C.

Zeit	0.10% Bi	0.010% Bi	0.0010% Bi	Banka
1	0	0	0	0
2	0	0	0	0
3	0	0	0	0
4	0	0	0	0
5	0	0	0	3
21	0	1	0	
25	0	3	3	
43	0			

B. Metalle, welche die Umwandlungsgeschwindigkeit des mechanisch deformierten Zinns beschleunigen.

6. Als wir eine Legierung von Banka-Zinn mit 1 % Zn bzw. mit 1 % Al, nachdem dieselbe die in § 2 genannte mechanische Deformierung durchgemacht hatte, einer Temperatur von  $-50^{\circ}$  C. unterwarfen, trat die Zinnpest bereits nach einigen Stunden ein.

Diese Tatsache veranlasste uns die betreffenden Versuche in ausgedehntem Masstabe auszuführen. Die Tabellen 3 und 4 enthalten die Ergebnisse, welche nunmehr ohne Weiteres verständlich sein dürften.

Bereits sehr geringe Zn- bzw. Al-Zusätze beschleunigen die Umwandlung ganz enorm, sodass bereits nach einigen Tagen die betreffenden

TABELLE 3.  
Temperatur  $-50^{\circ}$  C.

Zeit	10% Zn	0.50% Zn	0.10% Zn	0.050% Zn	0.010% Zn	Banka
1	0	0	1	3	0	0
2	0	0	3		1	0
3	0	0			1	0
4	0	0			1	0
5	3	3			3	0
6						0
7						1
8						3

TABELLE 4.  
Temperatur  $-50^{\circ}$  C.

Zeit	0.50% Al	0.10% Al	0.050% Al	0.010% Al	Banka
1	3	3	3	3	0
2					0
3					0
4					3

Drähte völlig zu grauem Pulver zerfallen waren, während das reine Zinn die Zinnpest bei der nämlichen Temperatur ( $-50^{\circ}$  C.) nur an einzelnen Stellen zeigte.

Bei der Zinklegierung tritt ausserdem die interessante Erscheinung auf, dass diejenige mit 0.05 % Zink ein Maximum der Umwandlungsgeschwindigkeit aufweist. Wie die Tabelle 5 zeigt, tritt auch bei  $0^{\circ}$  C. dieselbe Erscheinung auf.

TABELLE 5.  
Temperatur  $0^{\circ}$  C.

Zeit	1% Zn	0.50% Zn	0.10% Zn	0.050% Zn	0.010% Zn	Banka
1	0	0	0	0	0	0
4	0	0	0	2	0	0
5	0	0	0	3	0	0
18	0	0	2		0	0
36	0	0	3		0	0
39	0	1			0	0
47	0	3			0	0
62	0				0	0

7. Wir haben die Umwandlungsgeschwindigkeit der Zinn-Zink bzw. Zinn-Aluminium-Legierungen, welche 0.05 % des betreffenden Fremdmetalls enthalten, auch bei *verschiedenen* Temperaturen studiert. Die Ergebnisse findet man in den Tabellen 6 und 7 verzeichnet.

Die beschleunigende Wirkung des Zn bzw. des Al tritt bei allen Temperaturen zu Tage. So trat bei der Legierung des Zinns, welche 0.05 % Al enthielt, bei  $0^{\circ}$  C. bereits nach 4 Tagen die Zinnpest auf, während das reine Zinn, welches dieselbe mechanische (thermische) Vorgeschichte hatte, selbst nach 27 Tagen noch keine Spur derselben zeigte.

TABELLE 6.

Zeit	0° C.		-11° C.		-22° C.		-50° C.	
	0.05% <sub>0</sub> Zn	Banka	0.05% <sub>0</sub> Zn	Banka	0.05% <sub>0</sub> Zn	Banka	0.05% <sub>0</sub> Zn	Banka
1	0	0	0	0	0	0	3	0
2	0	0	3	0	3	0		0
3	0	0		0		0		0
4	3	0		0		3		3
7		0		1				
8		0		1				
13		0		3				
27		0						

TABELLE 7.

Zeit	0° C.		-11° C.		-22° C.		-50° C.	
	0.05% <sub>0</sub> Al	Banka	0.05% <sub>0</sub> Al	Banka	0.05% <sub>0</sub> Al	Banka	0.05% <sub>0</sub> Al	Banka
1	0	0	1	0	3	0	3	0
2	0	0	3	0		0		3
4	1	0		0		3		
5	2	0		0				
6	2	0		0				
7	2	0		0				
8	3	0		3				

8. Die hier beschriebenen Geschwindigkeitsmessungen lassen sich zu scharf quantitativen verfeinern, indem man die Umwandlung der betreffenden Legierungen dilatometrisch verfolgt in der Art und Weise, wie früher<sup>1)</sup> von uns eingehend beschrieben wurde. Wir beabsichtigen darauf in Bälde zurückzukommen, wobei wir auch den Einfluss geringer, gleichzeitiger Zusätze mehrerer Metalle in besprechen gedenken.

#### *Zusammenfassung.*

Es wurde der Einfluss von Beimengungen fremder Metalle auf die Umwandlungsgeschwindigkeit von weissem Zinn bekannter mechanischer

<sup>1)</sup> Z. physik. Chem. A **173**, 1 (1935).



und thermischer Vorgeschichte studiert. Dabei stellte sich heraus, dass bereits äusserst geringe Mengen *Pb*, *Sb*, *Bi*, *Cd* oder *Ag* diese Geschwindigkeit herabsetzen, während *Zn* oder *Al* dieselbe enorm beschleunigen. Im Falle des Zinks wurde ein Maximum der Umwandlungsgeschwindigkeit bei einem Gehalte von 0.05 % festgestellt.

VAN 'T HOFF-Laboratorium.

Utrecht, Februar 1936.

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**Chemistry.** — *Der negative Ausdehnungskoeffizient des Jodsilbers.* Von ERNST COHEN und H. L. BREDÉE.

(Communicated at the meeting of February 29, 1936).

1. Bekanntlich entdeckte FIZEAU<sup>1)</sup> 1867 die merkwürdige Tatsache, dass das Jodsilber in dem Temperaturintervall  $-10$  bis  $+70^{\circ}\text{C.}$  einen negativen Ausdehnungskoeffizienten aufweist. Mittels eines sehr genauen optischen Verfahrens stellte er denselben (bei etwa  $40^{\circ}\text{C.}$ ) auf  $-4.1 \times 10^{-6}$  fest.

GRINNELL JONES und FREDERIC C. JELEN haben es sich in einer vor kurzem ausgeführten Untersuchung<sup>2)</sup> zur Aufgabe gestellt die Zuverlässigkeit dieser Daten mittels eines neuen Verfahrens zu prüfen und die Ausdehnung mehrerer analogen Salze zu ermitteln in der Hoffnung einem zweiten derartigen Fall auf die Spur zu kommen. Das Ergebnis ihrer Bestimmungen am Silberjodid geht dahin, dass zwischen  $20$  und  $60^{\circ}\text{C.}$  der kubische Ausdehnungskoeffizient desselben  $-1.6 \times 10^{-6}$  beträgt, ein Wert, welcher somit 2.5 Mal so gering ist als der von FIZEAU gefundene.

2. Zweck der nachstehenden Zeilen ist darzutun, dass die von den genannten amerikanischen Autoren getroffenen Fürsorgen nicht den Anforderungen Genüge leisten, welche nach dem heutigen Stande unserer Kenntnisse auf diesem Gebiete zu stellen sind und dass demzufolge ihre Ergebnisse dem Tatbestande nicht entsprechen.

3. Von ERNST COHEN und seinen Mitarbeitern<sup>3)</sup> wurde qualitativ

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<sup>1)</sup> Compt. rend. **64**, 314, 771 (1867); auch Pogg. Ann. **132**, 292, 303 (1867). Auch RODWELL (Chem. News **30**, 288 (1874); **31**, 5 (1875); Proc. Roy. Soc. **23**, 97 (1875); **25**, 280 (1877); **31**, 291 (1881)) fand, dass Jodsilber sich beim Erwärmen zusammenzieht. Seine quantitativen Bestimmungen sind indes nur orientierender Natur und können hier somit ausser Betracht gelassen werden.

<sup>2)</sup> J. Am. Chem. Soc. **57**, 2532 (1935).

<sup>3)</sup> Die Metastabilität der Elemente und Verbindungen als Folge von Enantiotropie oder Monotropie I—XVIII, Z. physik. Chem. (1920—1934). Auch Physico-Chemical Metamorphosis and some problems in Piezochemistry, 2nd edition, New-York and London (1928). Deutsche Ausgabe, Leipzig (1927).

sowie quantitativ der Nachweis erbracht, dass die festen Stoffe, welche wir täglich manipulieren, metastabile Gemische sind der Modifikationen, in denen dieselben aufzutreten im stande sind. Demzufolge kann den physikalisch-chemischen Konstanten jener Stoffe, welche, wenn auch chemisch rein, physikalisch unrein sind, eine Bedeutung nicht zugesprochen werden.

4. Auch das Silberjodid wurde nach dieser Richtung eingehend studiert, wobei sich herausstellte, dass, wie Tabelle 1 zeigt, die Werte, welche von verschiedenen Forschern für die Volumänderung gefunden wurde, welche die Umwandlung  $\alpha\text{-AgJ} \rightarrow \beta\text{-AgJ}$  (bei  $145.7^\circ \text{ C.}$ ) begleitet, Differenzen von mehreren Hundert Prozenten aufweisen.

Nur wenn die betreffenden Objekte sowohl chemisch wie physikalisch rein sind, erhält man scharf definierte, reproduzierbare Werte, wie die letzten drei Zahlen der Tabelle dartun.

5. Die in der Tabelle unter 6 und 7 vermerkten Untersuchungen haben nun ergeben, dass das aus wässriger Silbernitratlösung mittels wässriger Jodkaliumlösung gefällte  $\text{AgJ}$  aus einem Gemisch- der  $\alpha$ - und  $\beta$ -Modifikation besteht.

TABELLE 1.

Autorname	Volumänderung in $\frac{\text{cm}^3}{\text{g}}$
RODWELL <sup>1)</sup> (1882) . . . . .	— 0.0034
MALLARD und LE CHATELIER <sup>2)</sup> (1883) . . . . .	— 0.0193
TAMMANN <sup>3)</sup> (1911) . . . . .	— 0.0100
BENEDICKS <sup>4)</sup> (1912) . . . . .	— 0.0091
BRIDGMAN <sup>5)</sup> (1915) . . . . .	— 0.0086
COHEN und VAN DOBBENBURGH <sup>6)</sup> (direktes Verfahren). .	— 0.0094 <sup>2</sup>
Dieselben <sup>6)</sup> (indirektes Verfahren) . . . . .	— 0.0094 <sup>8</sup>
COHEN und BREDÉE <sup>7)</sup> (Gasvolumenometrisch). . . . .	— 0.0094 <sup>5</sup>

Handelt es sich um die Darstellung eines chemisch und physikalisch reinen Präparates, so ist das in oben erwähnter Weise gefällte Material zu schmelzen und sodann auf Zimmertemperatur abzukühlen. Dabei bildet

<sup>1)</sup> Chem. News **31**, 5 (1875).

<sup>2)</sup> Compt. rend. **97**, 102 (1883); Bull. Soc. Min. de France **6**, 181 (1883); Compt. rend. **99**, 157 (1884); Bull. Soc. Min. de France **7**, 478 (1884); J. phys. (2) **4**, 305 (1885).

<sup>3)</sup> Wied. Ann. Phys. **68**, 629 (1899); Z. physik. Chem. **75**, 733 (1911).

<sup>4)</sup> J. Iron Steel Inst. London **86** (2), 247 (1912).

<sup>5)</sup> Proc. Amer. Acad. Arts Sciences **51** (2), 55 (1915).

<sup>6)</sup> Z. physik. Chem. A **137**, 289 (1928).

<sup>7)</sup> Z. physik. Chem. A **140**, 199 (1929).

sich quantitativ  $\alpha$ -AgJ, dessen physikalisch-chemische Konstanten völlig definiert und reproduzierbar sind.

6. GRINNELL JONES und FREDERIC C. JELEN teilen über das von ihnen verwendete Silberjodid folgendes mit: "Silver iodide was precipitated from a nitrate solution by the addition of potassium iodide solution".

Da sie das von ihnen studierte Objekt nicht vorher der Schmelzung unterwarfen, haben sie die Bestimmung des Ausdehnungskoeffizienten somit an einem physikalisch unreinen Material ausgeführt. Der gefundene Wert  $-1.6 \times 10^{-6}$  ist demnach als ein zufälliger zu betrachten, dem keine Bedeutung zukommt.

7. Dass die genannten Autoren einen numerisch zu niedrigen Wert finden würden, lässt sich auf Grund folgender Ueberlegung voraussagen: Nach den oben (Tabelle 1 unter 6 und 7) aufgeführten Messungen ist die Umwandlung  $\beta$ -AgJ  $\rightarrow$   $\alpha$ -AgJ von einer Volumzunahme begleitet. Wandelt sich bei den Messungen des Ausdehnungskoeffizienten (welche von JONES und JELEN zwischen 20 und 60° C. ausgeführt wurden) das vorhandene metastabile  $\beta$ -Jodid in das stabile  $\alpha$ -Jodid um, so wird der gefundene negative Ausdehnungskoeffizient zu klein. Tatsächlich fanden JONES und JELEN einen viel geringeren Wert ( $-1.6 \times 10^{-6}$ ) als FIZEAU ( $-4.1 \times 10^{-6}$ ) und wie sich sogleich ergeben wird, hat Letzterer chemisch und physikalisch reines  $\alpha$ -AgJ zu seinen Messungen verwendet.

8. Dass dem so ist, ergibt sich aus der Mitteilung FIZEAUS, dass er zu den betreffenden Messungen Objekte benutzte, welche nach dem Fällen aus einer Silbernitratlösung mittels einer Jodkaliumlösung zuvor geschmolzen gewesen, bezw. nach dem Schmelzen und Erstarren noch während 4 Stunden bei 100° C. getempert waren.

Das von ihm verwendete Material war also das bei den Versuchstemperaturen auch physikalisch reine, stabile  $\alpha$ -Silberjodid.

Bis auf Weiteres ist somit dem von FIZEAU ermittelten Werte  $-4.1 \times 10^{-6}$  (bei 40° C.) volles Zutrauen entgegenzubringen.

#### *Zusammenfassung.*

Es wurde nachgewiesen, dass der Neubestimmung des negativen Ausdehnungskoeffizienten des  $\alpha$ -AgJ seitens GRINNELL JONES und FREDERIC C. JELEN ein Fehler von mehreren Hundert Prozenten anhaftet infolge der Verwendung von *physikalisch* unreinem Material.

Utrecht, VAN 'T HOFF-Laboratorium.

Februar 1936.

Breda, Laboratorium der Hollandsche Kunstzijde Industrie, N.V.

**Chemistry.** — *Studien über Korrosion.* Von ERNST COHEN und W. A. T. COHEN—DE MEESTER.

(Communicated at the meeting of February 29, 1936).

*Einleitung.*

Das grosse Interesse, welches man der unter dem Namen „Korrosion“ bekannten Erscheinung entgegengebracht hat, tritt nicht nur darin zu Tage, dass zahllose Einzelforscher sich bereits seit HUMPHRY DAVYS Zeiten mit dem Studium derselben befasst haben, sondern auch in der Tatsache, dass sich in neuerer Zeit in fast allen Kulturländern Vereine gebildet haben, welche sich der Spezialforschung nach den Ursachen dieses unliebsamen Phänomens, welches jährlich Millionen verschlingt, widmen. Dabei spielt selbstverständlich der Wunsch Mittel zur Bekämpfung dieses Schmerzenskindes der Technik ausfindig zu machen, die Hauptrolle.

Dementsprechend hat die Literatur auf diesem Gebiete derartige Dimensionen angenommen (es liegen bereits mehr als 10.000 Abhandlungen über diesen Gegenstand vor), dass es sich als notwendig herausstellte die Titel derselben in einem Spezialwerke zusammenzufassen.

Bezeichnend für den heutigen Tatbestand ist die Aeusserung von W. H. J. VERNON <sup>1)</sup>, des Verfassers einer solchen Literaturübersicht: „In compiling this bibliography I have been impressed by the enormous amount of energy that has been expended in duplicating the work of others“.

Wenn wir uns unter diesen Verhältnissen dennoch dem Studium der Korrosion zugewandt haben, geschah dieses auf Grund der Ueberlegung, dass die neuerdings durch die Untersuchungen von ERNST COHEN, W. A. T. COHEN—DE MEESTER und A. K. W. A. VAN LIESHOUT <sup>2)</sup> zu Tage geförderten Tatsachen über den Einfluss mechanischer Deformation auf die Geschwindigkeit polymorpher Umwandlungen selbstverständlich bisher beim Studium der Korrosion nicht in Betracht gezogen werden konnten.

Nun haben die Studien von ERNST COHEN und seiner Mitarbeiter <sup>3)</sup> zu dem Schlusse geführt, dass Polymorphie eine allen Stoffen gemeinsame Eigenschaft ist und dass infolge der starken Verzögerungen, welche die Umwandlungen verschiedener Modifikationen eines selben Stoffes begleiten, die Elemente und Verbindungen, denen wir im täglichen Leben gegen-

<sup>1)</sup> A Bibliography of metallic corrosion. London, EDWARD ARNOLD & Co. (1928).

<sup>2)</sup> Z. physik. Chem. A **173**, 1, 67, 169 (1935). Proc. Royal Acad. Amsterdam, **38**, 377 (1935).

<sup>3)</sup> Die Metastabilität der Elemente und Verbindungen als Folge von Enantiotropie oder Monotropie I—XVIII. Z. physik. Chem. (1920-1934). Auch Physico-Chemical Metamorphosis and some problems in Piezochemistry, 2nd edition, New-York and London (1928). Deutsche Ausgabe, Leipzig (1927).



überstehen, metastabile Gemische solcher Modifikationen sind, welche sich somit in steter Umwandlung befinden.

Es liegt auf der Hand die Erscheinung der Korrosion von den neu gewonnenen Standpunkten näher zu betrachten und zu untersuchen ob sich von dortaus eine Erklärung für das Auftreten derselben geben lässt.

Zunächst war festzustellen ob ein heute vielfach verwendetes Verfahren zur Messung der Korrosionsgeschwindigkeit den Anforderungen genügt, welche man an ein solches zu stellen hat, falls es sich um die Erzielung genauer, reproduzierbarer Daten handelt, während eventuell andere Verfahren nach dieser Richtung zu prüfen waren. Die vorliegende Abhandlung enthält unsere diesbezüglichen Versuche.

### *Die Reproduzierbarkeit von Korrosionsbestimmungen.*

1. Ein selbst bei den jüngsten Untersuchungen über Korrosion noch immer befolgtes Verfahren gestaltet sich folgendermassen, falls es sich z.B. um das Studium der Korrosion von reinem Zinn durch verdünnte Salzsäure (0.1 n.) bei gegebener Temperatur (25.00° C.) handelt: Bei Zimmertemperatur gewalzte Plättchen ( $6.5 \times 2.5$  cm) werden mit feinem Schmirgelpapier abgerieben, mittels Tetrachlorkohlenstoffs entfettet und in trockner Luft über Chlorkalcium während 24 Std. im Exsikkator aufbewahrt bevor dieselben der Korrosion ausgesetzt werden. Sodann hängt man die zu untersuchenden Plättchen, jedes für sich, nachdem deren Einzelgewicht bestimmt ist, vertikal und symmetrisch in Bechergläser aus Jenaglas (mit vertikaler Wand) von 4 cm Durchmesser, deren Höhe 8 cm beträgt. Jede Platte hängt an einem Papierbinder, welcher von einem Glasstab getragen wird, der auf dem Rande des Becherglases liegt und mittels Wachs in fester Lage gehalten wird. Der in die Flüssigkeit (0.1 n. HCl) tauchende Teil der Platten hat eine Oberfläche von  $3.5 \times 2.5$  cm<sup>2</sup>. Die Bechergläser stellt man in ein Exsikkatorgefäß von 5.5 L. Inhalt, welches in einem Thermostaten auf 25.00° C. gehalten wird. Jeden Tag erneuert man die Luft im Exsikkator.

2. Nach 6 Tagen unterwirft man die Platten der Wägung, nachdem dieselben getrocknet waren. Falls sich ein Korrosionsprodukt auf den Platten nicht gebildet hatte, wurde der Gewichtsverlust derselben als ein Mass für die Korrosionsgeschwindigkeit betrachtet. Es werden mit dem betreffenden Material Doppelversuche angestellt und das Mittel der Ergebnisse derselben legt man den Betrachtungen zu Grunde, welche sich an die betreffenden Versuche knüpfen, die in dem hier erörterten Falle den Vergleich zwischen der Korrosionsgeschwindigkeit des Zinns in 0.1 n. Salzsäure bei 25.00° C. mit derjenigen in anderen Medien bei derselben Temperatur zum Zweck hatten.

3. Wir haben das hier erörterte Verfahren einer Kontrolle unterworfen, indem wir dem soeben beschriebenen Wege *bis in Einzelheiten*

folgten mit dem Unterschiede jedoch, dass wir statt *Doppelversuche* solche anstellten, wobei 8 Platten unter möglichst identischen äusseren Verhältnissen gleichzeitig der Korrosion ausgesetzt wurden. Unsere Tabelle 1 enthält die betreffenden Versuchsergebnisse. Dieselbe zeigt, dass es unzulässig ist aus dem Ergebnis von Doppelversuchen den Wert der Korrosionsgeschwindigkeit ohne Weiteres abzuleiten, selbst in Fällen, worin, wie hier, grösste Sorgfalt auf die gleichmässige Vorbereitung sämtlicher Platten verwendet wurde.

TABELLE 1.

Temperatur 25.00° C.

Korrosion von Zinnplatten (Banka-Zinn) von  $6.5 \times 2.5$  cm in 0.1 n. HCl.Die untergetauchte Oberfläche beträgt  $3.5 \times 2.5$  cm.Korrosionszeit  $6 \times 24$  Std.

Versuchsnummer	Gew. in g vor dem Versuch	Gew. in g nach dem Versuch	Gewichtsverlust in mg	Abweichung vom Mindestwert in ‰	Abweichung vom Mittelwert in ‰
1	13.2492	13.2038	45.4	5	— 3.5
2	13.5782	13.5278	50.4	15	+ 7
3	13.0827	13.0258	56.9	27	+20
4	13.2305	13.1872	43.3	0	— 8
5	13.3155	13.2719	43.6	0.6	— 7.5
6	13.4445	13.3985	46.0	6	— 2
7	13.3702	13.3241	46.1	6	— 2
8	13.3782	13.3336	44.6	3	— 5

4. Bei den in § 3 erörterten Versuchen kam, da nicht gerührt wurde, die Erneuerung der korrodierenden Säure an der Oberfläche der Zinnplatten durch Diffusion zu stande. Wir wandten uns nunmehr der Lösung der Frage zu, ob sich durch Rühren eine grössere Reproduzierbarkeit erzielen liess. Die betreffenden Versuche gestalteten sich folgendermassen: In einem Becherglase aus Pyrexglas gossen wir uns Zylinder aus reinem Banka-Zinn, welche 2 cm hoch waren und einen Durchmesser von 7 cm hatten. Aus einem solchen Zylinder wurden bei Zimmertemperatur zwei Platten gewalzt, deren Höhe, Breite und Dicke bezw. 10, 9 und 0.1 cm betrugen. Sodann bogen wir die beiden Platten zu Zylindern, die der Höhe entlang einen mehrere Millimeter weiten Schlitz hatten, dessen Kanten nach aussen gebogen waren, sodass dieselben als Rührer fungierten, wenn man die in die Säure eingetauchten Zylinder um deren Achse rotieren liess.

Die so vorbereiteten Zylinder schmolzen wir, jeden für sich, in ein hochvakuiertes Glasrohr ein und hielten die Rohre, zwecks Temperung des

Zinns, während  $6 \times 24$  Std. im Trockenschrank auf etwa  $160^\circ \text{C}$ . Sodann erfolgte langsame Kühlung und schliesslich Entfettung der Zylinder durch Abwaschen mit Aether.

5. Jeden der beiden Zylinder brachten wir nunmehr in einen Apparat

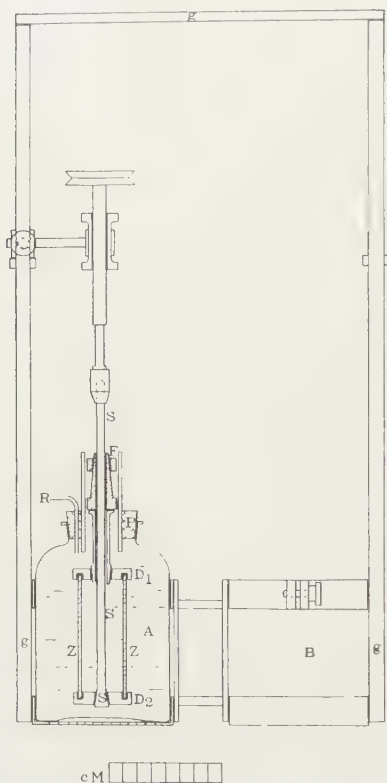


Fig. 1.

(Fig. 1), der uns in stand setzt dieselben mit der gleichen Geschwindigkeit in der korrodierenden Flüssigkeit rotieren zu lassen, wobei jede Berührung des Zinns mit irgendwelchem Fremdmetall ausgeschlossen war. Wir erreichten dies mittels der in Fig. 1 abgebildeten Vorrichtung: In einem Messinggestell *G* stehen zwei möglichst identische, weithalsige (etwa 600 cc. fassende) Flaschen *A* und *B* aus Jenaglas, welche fast ganz mit 0.1 n. HCl gefüllt sind. Durch den Gummipfropfen *PP* ist ein Glasstab *SSS* geführt, welcher zwei schwere Glasplatten *D*<sub>1</sub> und *D*<sub>2</sub> trägt, zwischen welchen der Zinnzylinder *ZZ* mittels der Schraubvorrichtung *F* (aus Hartgummi) eingeklemmt ist. Der Zylinder steht an seinem oberen und unteren Ende in Rillen, welche in die Glasplatten geschliffen sind. Der Glasstab *SSS* fungiert als Achse, welche von einem Elektromotor in drehende Bewegung versetzt wird. Es war dafür gesorgt, dass die in den Flaschen *A* und *B* völlig untergetauchten

Zylinder stets dieselbe Geschwindigkeit (etwa 100 Touren pro Minute) hatten. Der obere Teil von *A* und *B*, welcher nicht mit der Säure gefüllt war, enthielt Stickstoff, der durch ein Glasrohr, welches den Pfropfen *PP* durchsetzt, aus einer Bombe in äusserst langsamem Tempo in die Flasche geleitet wurde. Mittels spezieller Versuche stellten wir fest, dass die Konzentration der Salzsäure während der Dauer der Korrosion durch den verwendeten Gasstrom eine Aenderung nicht erfuhr. Während der Korrosion standen beide Flaschen in dem Gestell in einem grösseren Wasserthermostaten (Temp.  $10^\circ \text{C}$ .). In beide Flaschen gaben wir vor dem Versuch 550 cc. 0.1 n. Salzsäure und ermittelten nach der Korrosion deren Gehalt an gelöstem Zinn durch Titrieren (mit 1/20 n. Jodlösung) nach dem von KOLTHOFF und VAN DER HEYDE<sup>1)</sup> beschriebenen Verfahren, nachdem wir dasselbe auf seine Zuverlässigkeit geprüft hatten. In vier

<sup>1)</sup> Z. analyt. Chem. 60, 452 (1921); KOLTHOFF, die Massanalyse II, 393, Berlin (1928).

Versuchen ergab die Analyse bei Verwendung eingewogener Zinnmengen (reinstes Banka-Zinn) Abweichungen vom Sollwerte, welche bezw.  $-0.5$ ;  $-0.6 + 0.6$  und  $-0.1\%$  betrugen, d.h., dass die Genauigkeit für unsere Zwecke völlig ausreichte.

6. In dieser Weise vorgehend, erhielten wir die in Tabelle 2 verzeichneten Werte.

TABELLE 2.  
Temp.  $10^{\circ}$  C.  
Korrosion von rotierenden Zinnzylindern von  $180\text{ cm}^2$  Oberfläche in  
 $0.1\text{ n. HCl}$  (4 Std.).

In Lösung gegangen	
mg Zinn	
A	803.4
B	1799.1

Auch bei Verwendung dieses Verfahrens lässt sich somit aus Doppelversuchen ein Schluss nicht ziehen.

7. Als wir einen solchen Zinnzylinder in zwei gleiche Teile zerschnitten und die beiden Hälften in den Flaschen A und B in der in § 5 beschriebenen Art und Weise der Korrosion unterwarfen, fanden wir nach gleichen Zeiten für die eine Hälfte eine Gewichtsabnahme von 25.8, für die andere eine solche von 16.3 mg. Auch bei diesem Rotationsverfahren ist es somit unzulässig aus Doppelversuchen irgend welchen Schluss zu ziehen.

8. Dasselbe ergab sich, als wir statt eines Zinnzylinders je 8 rotierende Zinnstäbe, welche möglichst identisch vorbehandelt waren, in jeder Flasche der Korrosion durch Salzsäure aussetzten. Die in Doppelversuchen erhaltenen Gewichtsverluste (in mg) betrugen 102.3 und 101.3; 122.7 und 322.5; 228.6 und 117.45; 98.8 und 287.

### *Zusammenfassung.*

Es wurde nachgewiesen, dass nicht nur ein sehr beliebtes Verfahren zur Bestimmung der Korrosionsgeschwindigkeit von Metallen, wobei die korrozierende Flüssigkeit sich an der Metalloberfläche durch Diffusion erneuert, so stark wechselnde Werte liefert, dass es unzulässig ist hierbei aus Doppelversuchen Schlüsse über die genannte Geschwindigkeit zu ziehen, sondern dass dasselbe gilt, falls die Erneuerung mit grosser Geschwindigkeit durch Konvektion stattfindet.

VAN 'T HOFF-Laboratorium.

*Utrecht*, Februar 1936.



**Chemistry.** — *On the Localization of the Transition-points of Allotropic Metals under varied Circumstances by Means of the Method of*  
SALADIN—LE CHATELIER. By E. ROSENBOHM and F. M. JAEGER.

(Communicated at the meeting of February 29, 1936).

§ 1. In connection with our investigations, within an interval of  $100^{\circ}$ — $1600^{\circ}$  C., on the dependence of the specific heats of metals on the temperature, it gradually proved ever more desirable to check the calorimetrically established localization of the transition-points of the reversible allotropic changes occasionally observed in such metals by means of a quite independent method which, moreover, would enable us to study also some other physical properties of those metals in function of their temperatures.

Such a method, well suited for the purpose, was found by using, in a somewhat modified form, the principle suggested by SALADIN in 1903 and first applied by LE CHATELIER a.o. in metallurgical investigations<sup>1)</sup>, because it not only is applicable to the determination of heating-curves in the thermal analysis and to the detection of transformation-temperatures, but, — as later on we will demonstrate, — it is more especially suited for the study of the temperature-coefficient of the electrical resistance of such metals, as well as for that of their thermoelectrical properties. In this paper, however, we only wish to deal with some results obtained during our tentatives to localize the true transition-points just mentioned in the case of allotropic metals or polymorphous alloys, because these results, — more particularly with respect to the influence exerted by small amounts of gases present, — may prove to be of a general interest in all work of this kind.

§ 2. The principle of SALADIN consists in the use of two optically coupled galvanometers in combination with a photographic recording-device.

The two moving coil galvanometers, which in general have different but in rather wide limits adjustable sensitivities, are both steadily mounted upon the same vibrationfree and heavy support. A pencil of light emitted by a luminous source, — for instance by a small incandescent lamp, — first passes a screen provided with a small circular opening and then is reflected by the horizontally swinging mirror of the first, more sensitive

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<sup>1)</sup> H. LE CHATELIER, *Revue Métall.*, **1**, 134 (1904); conf. H. HARKORT, *Metall.*, **4**, 617 (1907); F. WEVER and K. APEL, *Mitt. Kaiser Wilhelm Instit. f. Eisenforschung*, **4**, 87 (1922); P. GOERENS, *Einführung in die Metallographie*, Halle, 198 (1932).

galvanometer; it subsequently passes an "inverting double prism", placed between the two galvanometers in such a way that the basal face of the prism is inclined under  $45^\circ$  with respect to the horizontal plane and thus to the surface of the first mirror, so that the originally *horizontal* motion of the reflected ray now is converted into a *vertical* one. This vertically moving luminous ray is subsequently reflected by the equally horizontally swinging mirror of the second galvanometer, the reflecting surface of which is about twice as large as that of the first mirror, so that the deflections of the latter may to their full extent eventually be utilized for the purpose of recording. The ray reflected from this second mirror finally reaches the photographic plate ( $13 \times 18$  cm), which is exposed to its action and is mounted in a camera of special construction; a system of lenses is adjusted in such a way, that a sharp, almost point-shaped image of the small circular opening in the diaphragm mentioned, placed closely behind the incandescent lamp, is produced, which, according to the combined horizontal and vertical motions of the pencil of light twice reflected, now will describe its resultant path over the photographic plate. A periodic interruption or weakening of the light-intensity of the ray, regulated by means of a clockwork, allows the indication of the time elapsed at every moment by the broken curve thus produced, simply by counting the number of its hiatus.

If the second, horizontally recording galvanometer during the experiment is compelled to yield deflections which in a regular way increase or decrease with the time elapsed, whilst the first galvanometer is placed within a circuit in which the variable quantity  $x$  to be measured is simultaneously inserted, — the path described by the luminous spot will afford the necessary information about all slow or rapid changes occurring in the magnitude of the variable quantity  $x$ , in their connection with the values of the horizontal, regularly varying parameter at each arbitrary moment.

§ 3. The second of the two galvanometers in the present experiments now is connected with the thermocouple indicating the furnace-temperature and its sensitivity adjusted so as to allow a complete survey of the special interval of temperatures desired.

In the present investigation the other instrument, the sensitivity of which is also carefully adapted to the temperature-measurements intended, is connected with a *differential-thermocouple*, for the purpose of indicating at each moment the *difference* in temperature of the sample studied and of a standard substance, both simultaneously being heated at the same constant temperature  $t$  in the vacuum-tube still to be described. If *no* temperature-difference between the two samples exists, the lightspot on the photographic film will describe a horizontal line parallel to the axis of the furnace-(tube-)-temperatures; but at the least difference in temperature occurring between the two samples, it will deviate from the

horizontal line in the one or in the opposite direction. With the necessary precautions, each sudden difference in the specific heats of the two samples thus will immediately be recorded; and if beforehand both galvanometers are carefully calibrated and the scale of the temperatures on the photographic plate is exactly fixed, the temperatures at which the said deviations occur may be sharply localized, as well as the approximate magnitude of the thermal effect observed is roughly estimated. As a standard of comparison, theoretically a metal should be chosen, the specific heats of which, as well as its dependence on the temperature, are not only exactly known, but are as comparable as possible; its mass and that of the sample to be studied must be chosen in such a way, that in the beginning both masses will require about the same heat-quantities for heating them at equal temperatures. In this way the slope of the curve on the film will not appear too steep, — provided that the dependence of the specific heats of both substances on the temperature be at least rather closely comparable.

Attention also must be given to a certain degree of similarity in the state of the surfaces of the two metals, as, especially at intermediate temperatures, the influence of a too different surface-radiation proved to make itself seriously felt.

§ 4. The vacuum-tube used in these experiments is represented in figure 1. It consists of a gas-tight mantle  $B$  of PYTHAGORAS-mass, at its upper end closed by a water-cooled gas-tight cover of brass, through which the thermocouple  $E_3$ , for measuring the furnace-temperature, as well as the wires of the differential-thermocouple  $E_1E_2$  pass under perfect isolation. Moreover, the inlets and outlets  $G$  for occasionally introducing a circulating gas flow, are also conducted through it. Perforated screens are adjusted in such a way as to ascertain the constancy of the temperature throughout the heated tube over the whole extent of the partition in which the objects to be compared are placed; moreover, these heated objects,  $M_I$  and  $Me_0$  are, carefully isolated, placed one above the other and surrounded by a vertically divided copper-mantle, so as to improve the equal distribution of the temperature throughout. This mantle too is at its upper end and at its bottom screened off by the diaphragmas  $S_B$  and  $S_0$ , the shape and perforation of these being indicated on the left in figure 1. The objects to be compared and the wires of the thermocouples, — the latter being enclosed in four crosswise arranged capillaries of PYTHAGORAS-mass, — are besides protected against contamination by copper-vapours at the highest temperatures ( $900^\circ$ — $1000^\circ$ ) by means of a cylinder of the same material. In the present case the metals studied usually had the shape of spheres of suitable dimensions and their specific heats, in their dependence on the temperature, were beforehand carefully studied.

If no special introduction of a gas is needed, the tube can by means of the tubes  $G$  be connected with an oil-pump of high exhausting power,

continuously being driven by an electromotor and allowing to maintain an almost constant vacuum (of about 0.001 mm or less) during arbitrarily

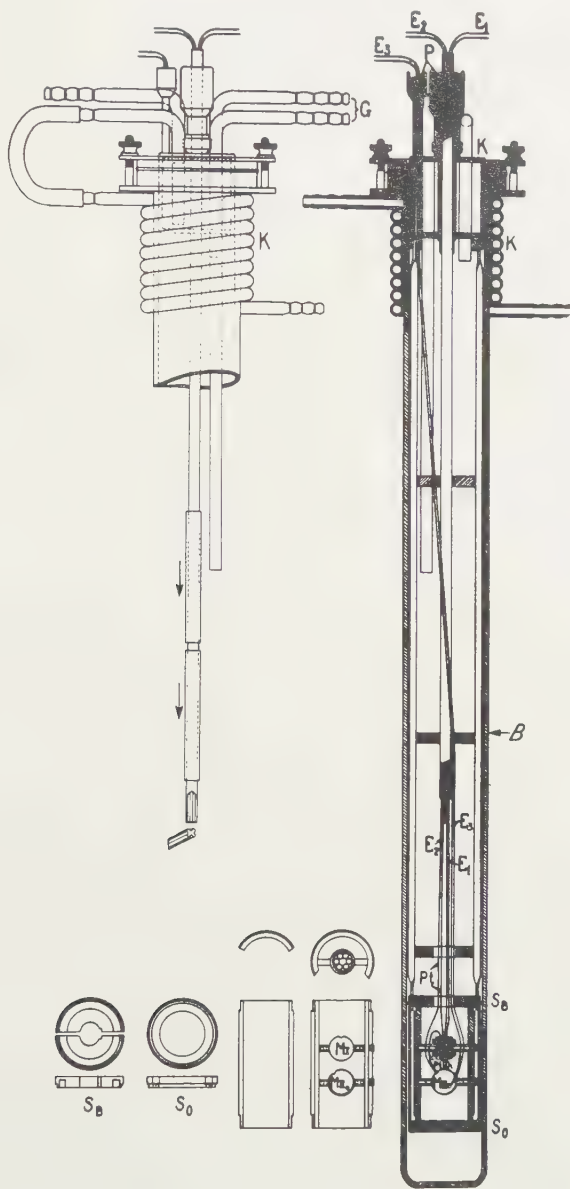


Fig. 1. Vacuum tube used in the Experiments.

long intervals of time; the vacuum produced was high enough to prohibit an electrical charge from passing through it. The whole tube is placed within an electrically heated furnace of the type always used in this laboratory, which, under the necessary precautions, allows a very accurate regulation and constancy of the temperature.

More especially the supplementary regulation of the furnace must be



avoided in the neighbourhood of the transition-points. For this reason the speed of heating must be chosen in such a way, that at least already a  $100^{\circ}$  beneath the transition-temperature a further change of the furnace-resistances is no more necessary.

The thermocouples were, of course, beforehand carefully calibrated in the usual way and their indications from time to time controlled and compared. In the course of the experiments, especially with those of long duration, it proved necessary to provide all stopcocks with mercury-fittings and to insert a vacuum-vessel of great capacity between the pump and the vacuum-tube, so as to protect the latter against sudden jumps of pressure.

§ 5. As to the calibration of the galvanometers used, it may be remarked that in our experiments the second horizontally recording galvanometer ordinarily had the lower sensitivity; it was used for the recording of the temperature of the heating-apparatus and of the sample to be investigated enclosed in it. As during the photographic record the motion of the luminous spot, of course, cannot visually be observed and the gradual increase of the temperature of the heated object has yet to be checked at each moment, we for this purpose used a method previously suggested by WEVER and APEL<sup>1)</sup>, but somewhat modified for the present occasion. The ends of the thermocouple, therefore, were not only connected with the galvanometer, but simultaneously with a moving coil pyrometer, indicating the temperature in degrees centigrade. As both instruments, however, in this way are used in *parallel* connection, the current produced by the thermocouple will be diminished by them in the ratio of their (unequal) resistances. As long as the external resistance applied to the galvanometer is sufficiently high, the error introduced in this way can readily be neglected; but if more exact measurements are made, — e.g. if the whole length of the photographic plate had to be used for only a short range of temperatures, — the external resistance of the now rather sensitive galvanometer must accordingly be diminished and in that case it is no longer allowed to cancel the said error. Therefore, in the latter case a second thermocouple was used instead of the pyrometer, so that the full sensitivity of the galvanometer now could be utilized: when the maximum sensitivity of the instrument was used, the whole length of 18 cm of the photographic plate proved to correspond to an interval of temperature of about  $150^{\circ}$  C., in the case that a *Pt-PtRh*-thermocouple is made use of. The calibration of the galvanometer (internal resistance: 15.4 Ohm) for intervals of  $300^{\circ}$ ,  $600^{\circ}$  and  $1000^{\circ}$  C. for the same length of the photographic plate must preliminarily be executed by inserting the suited external resistances; although the deflections of the instrument for these different external resistances were calibrated in the same way as by WEVER and APEL, — here the variable resistances of the circuit continuously needed to be taken into account, when we passed from the calibration-

<sup>1)</sup> F. WEVER and K. APEL, loco cit.



arrangement to the thermocouple itself. This was done by measuring the resistance of the thermocouple plus its supplying joints with an accuracy of 0.1 Ohm from 100° C. upwards at different temperatures between 100° 1000° C.; measured by the aid of a WHEATSTONE-bridge, it proved to increase from 4.2 to 5.6 Ohm. The final conversion of the thermoelectrical force  $E'$  of the thermocouple, measured (in Millivolts) into degrees centigrade, was made by measuring  $E'$  at 419° (mpt. of *zinc*), at 800° C. (mpt. of *NaCl*) and at 1063° C. (mpt. of *gold*), — these numbers being found in full agreement with the previously determined calibration-scale of both the thermocouples used. Still it must be remarked that on measuring within different intervals of temperature, e.g. from 0°—300°, from 300°—600°, from 600°—900° C., etc. — the zero-point of the galvanometer had, of course, every time to be shifted by a suitable rotation of the top-screw of the instrument <sup>1)</sup>.

§ 6. For the purpose of deducing the true temperatures on the photographic plate from the deflections registered, the plate must preliminarily be calibrated by imprinting calibration-marks upon it for a series of known temperatures or definite temperature-differences respectively. This was done by exposing the plate for a series of known temperatures to the short action (10 seconds) of a point-shaped light-spot, so that afterwards the corresponding calibration-marks got visible when the plate was finally developed.

Of course, the regulation of the sensitivities of the galvanometers by inserting varied external resistances in their circuits has to be made in such a way that, during the whole interval of temperatures studied, their deflections never will reach the borders of the photographic plate: this must be ascertained beforehand by a method of trial and error and, especially in the case of very irregularly occurring changes in the differential-curves obtained, in the beginning failures in this respect hardly can be avoided.

§ 7. *The Transition-point of Nickel.* As a first example of the applicability of the method described, the transition-point:  $\alpha$ -nickel  $\rightleftharpoons$   $\beta$ -nickel was more especially studied under various circumstances. A sphere of pure *nickel* of about 1 cm diameter was, in these experiments, compared with a suitable sphere of *copper* of about the same heat-capacity. As between 300° and 400° C. the temperature-coefficients of the specific heat  $c_p$  of the two metals are pretty accurately the same, it proved possible to make the temperature-difference between the two spheres, up to the transition-point, very small and regular indeed. Thus the first part of the

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<sup>1)</sup> Usually the photographic plate was used for 1000° C. over its whole length, but also intervals of smaller extent occasionally were studied with a corresponding alteration of the sensitivity of the galvanometers. For the purpose of shifting the zero-point of the galvanometer WEVER and APEL made use of an auxiliary current, but we have always avoided to do so.

heating-curve *A* in Fig. 2 is almost horizontal and the transition-point itself, therefore, is revealed as a very sharp discontinuance at 369°—



Fig. 2. Transition-point of Nickel, when heated or cooled in a Vacuum or in an Hydrogen-atmosphere of low Pressure.

370° C., when the experiment is made in a high vacuum. On the other hand we did not succeed in localizing the transition-point at the same spot by cooling down the wire under the same circumstances (*A'*): now it was always situated at a temperature about 6° lower than before; on rapid cooling even greater deviations proved to occur. If traces of gases, such as oxygen or hydrogen, were present under pressures ranging from 2 to 60 mm instead of a vacuum, a rather appreciable shift of the transition-temperature was observed in all cases, as may be seen from the curves *B* and *B'* in Fig. 2 obtained under a pressure of 50–60 mm of hydrogen. The transition-point now lies, on heating as well as on cooling, at 363°–364° C. and is in both cases practically identical. Within a pressure-interval of 2–60 mm this shift seems to be independent of the gas-pressure used. The data given in the literature about the localization of the transition-point:  $\alpha \rightleftharpoons \beta$ -nickel now are strongly divergent: they show differences as great as 20° C. It seems very likely that these discrepancies for a good deal may be caused by the presence of absorbed gases in the metal used in the various experiments.<sup>1)</sup>

<sup>1)</sup> However, attention must be drawn to the fact that, according to BREDIG, another (hexagonal) form (*a'*) of nickel, would be stable within the interval of 357° to 363° C.; conf. Proc. Royal Acad. Amsterdam, **34**, 818 (1931).

§ 8. *The Transition-points of the polymorphous Alloy: AuSb<sub>2</sub>.* As a second instance of transitions, this time in a polymorphous compound, the results of the determinations made with the binary compound AuSb<sub>2</sub><sup>1)</sup> are here communicated. Pure silver was used as the substance of comparison in this case and the experiments were executed in an atmosphere of hydrogen at low pressures. The two transition-points here were localized at 355° and 404° C. respectively, — in full agreement with the result previously obtained by means of the calorimetrical measurements<sup>1)</sup>. The curves represented in Fig. 3 clearly indicate that, on heating, a change evidently occurs at 355° C. different from that at the second transition-point of 404° C.: the first change evidently occurs almost instantaneously and the curve, after its sudden rise, rapidly falls back to almost the same height, as before the change took place. Suspicion might arise, that at this

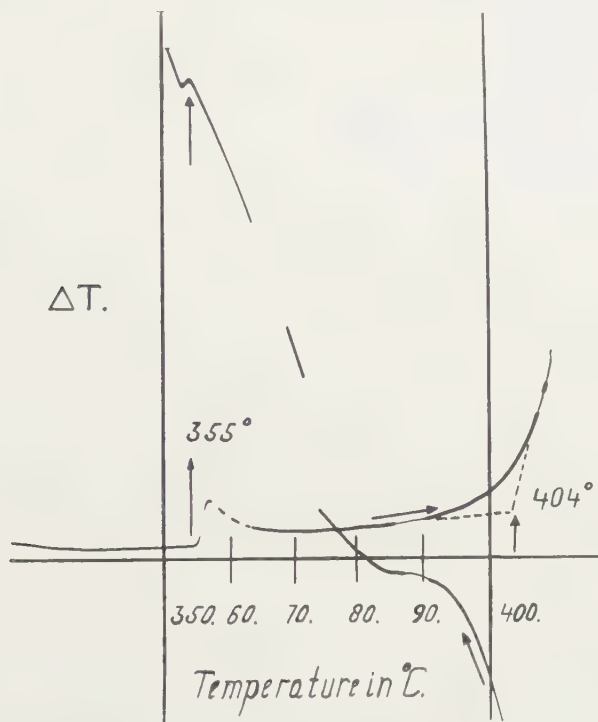


Fig. 3. *Transition-points of AuSb<sub>2</sub>.*

transition-temperature, where certainly a definite heat-effect occurs, the course of the temperature-coefficient of the specific heat  $c_p$ , after passing 355° C., truly remains the regular continuation of that before the change occurred. As the weights of the alloy and the silver used were known and the vertical deflections of the galvanometer were exactly calibrated, the

<sup>1)</sup> F. M. JAEGER and J. A. BOTTEMA, Proc. Royal Acad. Amsterdam, **35**, 916 (1932); Recueil d. Trav. d. Chim. d. Pays-Bas, **52**, 107, 108 (1933). The transition-points were calorimetrically determined to be: 355°.2 C. and 405° C.

size of the heat-effect involved could pretty accurately be determined from the measured height of the vertical deflection observed and was found to be: 0.3 calories per gramme of the alloy. Now from the calorimetric data for  $Q_0$  for the  $\gamma$ -modification previously determined, when extrapolated to temperatures between  $370^\circ$  and  $400^\circ$  C., it can be deduced that a *constant* difference of exactly 0.39 calories is found, when these values of  $Q_0$  for the  $\gamma$ -modification are diminished by those of the  $\beta$ -modification at the same temperatures. Evidently this constant difference is the heat of transition of the change:  $\beta \rightleftharpoons \gamma$ -modification and by this fact, indeed, it becomes highly probable that our suggestion, that practically *the same* temperature-coefficient of  $c_p$  may be attributed to the  $\gamma$ - as well as to the  $\beta$ -modification, is right.

At the other transition-point of  $404^\circ$  C., however, this certainly is *not* so; moreover, the latter transition:  $\beta \rightleftharpoons \alpha$ -modification occurs *much more slowly*, nor does the heating-curve exactly return to its previous height after the transition-point has once been surpassed. Because of the tardiness of this transition, even on cooling slowly, a strong hysteresis-effect is always observed, which is clearly expressed in the shape and situation of the cooling-curve with respect to that of the heating-curve; whilst on the other hand the change  $\beta \rightarrow \gamma$ -form, also on cooling, always proves to occur at practically the same temperature of  $355^\circ$  C. as before on heating.

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**Chemistry.** — *Measurement of the Electrical Resistance of Metals as Function of the Temperature by means of a Twin Galvanometer with Photographic Recording.* By E. ROSENBOHM and F. M. JAEGER.

(Communicated at the meeting of February 29, 1936).

§ 1. On dealing with the method of the determination of the differential-curves after the method of SALADIN—LE CHATELIER<sup>1</sup>), we already had an opportunity to make some general remarks concerning the possible applications of this method also for other purposes. As in the measurement of the *electrical resistance* in its function of the temperature, the same apparatus after some modifications proved to be equally suited to this special purpose, we here now will go into further details with respect to the necessary conditions to be fulfilled in these experiments, if trustworthy results in the measurement of the temperature-coefficient of the electrical resistance of metal-wires really shall be obtained.

<sup>1</sup>) E. ROSENBOHM and F. M. JAEGER, Proc. Royal Acad. Amsterdam, **38**, (1936).

The measurement of the temperature-coefficient mentioned seemed highly promising to us in connection with those of the specific heats of such metals in so far as, from a theoretical point of view, it might be expected that occurring abnormalities in the  $c_p$ - $t$ -curve at definite temperatures would show their replica at about the same temperatures in the curve representing the electrical resistance in its dependence on the temperature and vice-versa. Thus the real occurrence of such slow or sudden changes in the metals studied might in this way be rigorously checked by the comparison of the two independent series of data obtained. As it is of more importance for this control to make *comparative* experiments of this kind rather than to collect the exact *absolute* values of the properties thus studied, we have for our purpose again made use of the equipment previously described, but modified in the following way.

§ 2. For the measurements of the change of the electrical resistance of metal-wires in a high vacuum at various temperatures a WHEATSTONE-bridge (O. WOLFF) was used. However, instead of using it as a *zero*-instrument, the deflections of a galvanometer placed in the bridge-circuit and recorded on the photographic plate were measured and utilized for the intended purpose.

The metal-wire within the high-vacuum-tube was inserted in one of the side-branches of the WHEATSTONE-bridge, whilst the vertically recording galvanometer was placed in the diagonal shunt, i.e. in the bridge-circuit properly speaking. When the measuring device is initially compensated for a definite resistance, then the change of resistance of the metal-wire during its heating will produce certain deflections of the galvanometer, — for instance vertically upwards for an increase, downwards for a diminution of the wire-resistance; these deflections can at every moment be recorded on the photographic plate. If this change of resistance now should be measured for an interval, — let us say of  $500^\circ$ , — then the WHEATSTONE-bridge was initially compensated for a mean temperature of about  $250^\circ$ , in such a way that the beam of light for this special temperature made its impression exactly in the *midst* of the photographic plate, the current in the galvanometer now being *zero*: the instrument now will be over-compensated for lower and under-compensated for higher temperatures. For the purpose of deducing the special resistance of the heated wire at each moment from the deflections recorded on the photographic plate, the latter must preliminarily be provided with a series of calibration-marks by substituting the wire investigated by a variable, but accurately known auxiliary resistance of about the same magnitude. If, for instance, the resistance of the wire to be expected, for a deflection of the horizontally recording galvanometer corresponding to that resistance, were 1.5 Ohm in the middle of the plate, — then the WHEATSTONE-bridge was compensated for 1.5 Ohm at the very start of the experiment, so that



the current in the bridge-circuit then was zero, when the substituted variable resistance also was taken  $= 1.5$  Ohm; the vertically recording galvanometer, therefore, now showed *no* deflection. This point was fixed on the photographic plate by the short exposure (10 sec.) of the latter to a fine, point-shaped luminous source, the plate thus receiving an indication-mark for a current  $=$  zero and a resistance of 1.500 Ohm. When the whole measuring device now is kept constant, whilst only the variable resistance is systematically changed, the corresponding calibration-marks on the photographic plate could in just the same way be imprinted upon it for resistances of 1.4 Ohm, 1.3 Ohm, etc. and of 1.6 Ohm, 1.7 Ohm, etc. In this way the vertical co-ordinates of the curve were directly expressed in Ohms and the intermediate values, — after the subsequent development of the plate, — were finally found by calculation and graphical interpolation: the latter yielded sufficiently accurate results, as in most cases it proved to be an almost *linear* one to both sides from the fixed zero-point. The sensitivity of the recording galvanometer must, — by inserting suitable external resistances, — be regulated, of course, in such a way that within the whole interval of temperatures considered the vertical deflections never reach the extreme borders of the photographic plate: in the case of very irregularly and unexpectedly varying wire-resistances, — as e.g. with *titanium*, — this regulation is by no means an easy job, so that in the beginning many tentatives must be made before failures are completely avoided.

The method most advantageously furnishes data about the *variation* of the resistance with the temperature, rather than such for the absolute size of the latter; by changing the sensitivity of the recording galvanometer as well as the intensity of the current in the bridge, this variation of the resistance can, within wide limits, be made *independent* of the absolute magnitude of the resistance itself. If a photographic plate of  $13 \times 18$  cm is used, an exactness of 0.1 % of the variation mentioned can readily be attained. When the length of the plate available for the ordinates is 12 cm and, for instance, the change of the resistance within the temperature-interval studied is 1 Ohm, — then a variation of 0.001 Ohm corresponds to 0.12 mm or about the real breadth of the curve itself. By means of suitable filters placed before the luminous source, curves of very sharp and thin tracks can be obtained: we commonly used a yellow and red filter combined.

In WHEATSTONE'S bridge two different ways of connection are possible, as the places of the galvanometer and the electromotive force can be interchanged. The one method has the advantage of enabling the observer to use a very weak current, — which may be advisable in cases where the metal-wire is very thin and thus a heating of it by the current must be feared; the other involves the use of currents of all intensities and guarantees a higher independency for the observer from occasionally occurring thermoelectrical forces. For this reason we have always preferred

the latter way of connecting; the final elimination of such thermoelectrical forces will be dealt with more in detail further on.

In such complicated and capricious cases as in that of *titanium*, where several disturbing factors and retardation-phenomena play a role, the high degree of accuracy of the method can, of course, not nearly be attained. The method proved, however, most satisfactorily to meet with our requirements even in the complicated case mentioned. Its great advantage is that the curve desired need not to be built up from the determinations of singular points but is immediately recorded as an uninterrupted, *continuous* one, so that even small irregularities presenting themselves in it can never be overlooked.

§ 3. In the case of some metals difficulties are often met with concerning the way of producing the necessary contacts. Therefore, this was done in the following way, which proved to be applicable in almost all cases.

The supplying wires were of copper and had a diameter of 3 mm; at their ends they were hammered out over a length of about 2 cm and so flattened to about 1 mm thickness. At about 1 cm from the lower end they were perforated, the hole which was provided for having a boring somewhat less than the diameter of the *metal*-wire to be studied; this flattened end was subsequently bent in *U*-shaped fashion and the *metal*-wire pulled through the hole, upwards in the case of the one and downwards in that of the other copper-wire. Then both ends were tightly compressed, so that the *metal*-wire to be investigated was deeply impressed into the preliminarily heated and thus very soft copper terminals.

In this way a very good contact was guaranteed, which often even at 1000° C. proved to be excellently preserved.

Because of the oxidability of many metals the measurements must be made in a high vacuum. For this purpose a high-vacuum-tube, heated in an electrical furnace, was constructed, which remained gas-tight even at 1400° C. Its construction is in most respects quite similar to that described in our paper on the determination of the differential-curves previously published. It also consists of a gas-tight mantle of PYTHAGORAS-mass, closed at the upper end, — which emerges about 20 cm above the rim of the electrical furnace, — by a double-walled, water-cooled copper-cover, provided with a flange. Through this cover all supplies for the current, the pump-leads and the thermocouples pass; the space of constant temperature, in which the metal-wire, wound in the shape of a spiral, was freely hanging between the thick copper wires already mentioned, is about 6 cm high and is situated at the bottom end of the vacuum-tube. The about 3 cm long spiral is enclosed within a 2 cm thick mantle of copper or nickel and this space is limited also by an upper and a lower cover of the same metal. As in a high vacuum copper at the highest temperatures (1000°) readily volatilizes, the spiral must be protected against this by

screens and walls of PYTHAGORAS-mass: in Fig. 1 to the left the disconnected parts of the copper- and PYTHAGORAS-mantles are shown and to the right

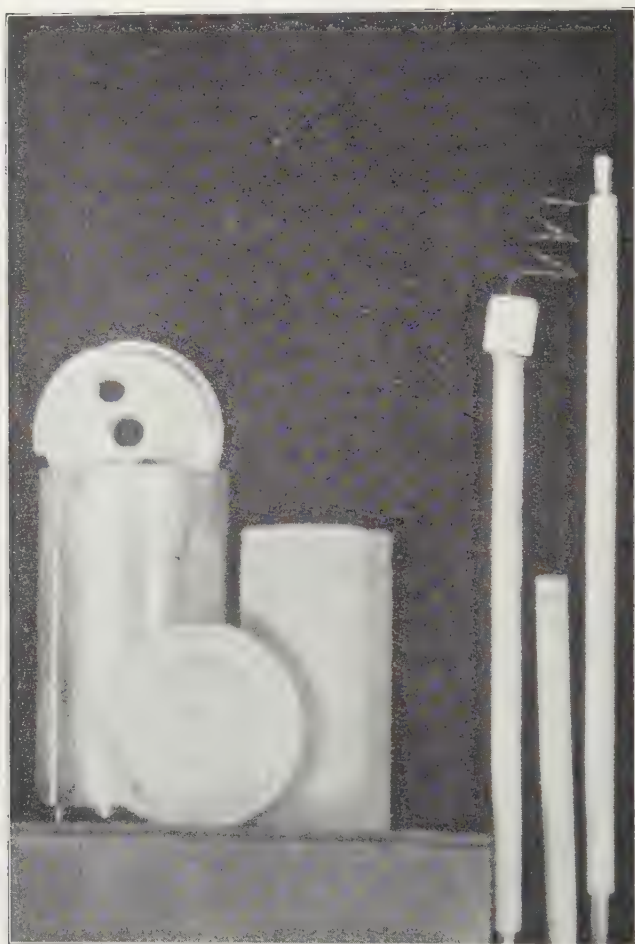


Fig. 1. To the left: Copper-mantle and mantle of PYTHAGORAS-mass in disconnected Parts. To the right: The Spiral Wire between Copper-wires, covered with Capillaries and one of the Cups.

the spiral of the wire between its copper leadings, protected by gas-tight capillaries and the ends by cups, so as to avoid a contamination by a deposit of volatilized copper. One of the cups is removed in the figure. Also the wires of the thermocouples had, for the same reason, to be covered by such capillaries. The copper mantle was supported by the copper bottom, which itself was held in position by a ring of nichrome, fixed by bearers connected with the flange at the upper end of the tube. A second ring, higher up in the tube, served as a device for centering and adjusting; between the bearers several diaphragmas of PYTHAGORAS-mass were inserted, so as to guarantee as much as possible the maintainance

of a homogeneous distribution of the temperature within the tube. The upper, water-cooled part of the tube consisted of a hollow copper cylinder ending in a flange with a fitting cover (Fig. 2); as it has several perforations for the different inlets, it had to be soldered with a hard solder<sup>1)</sup> and,

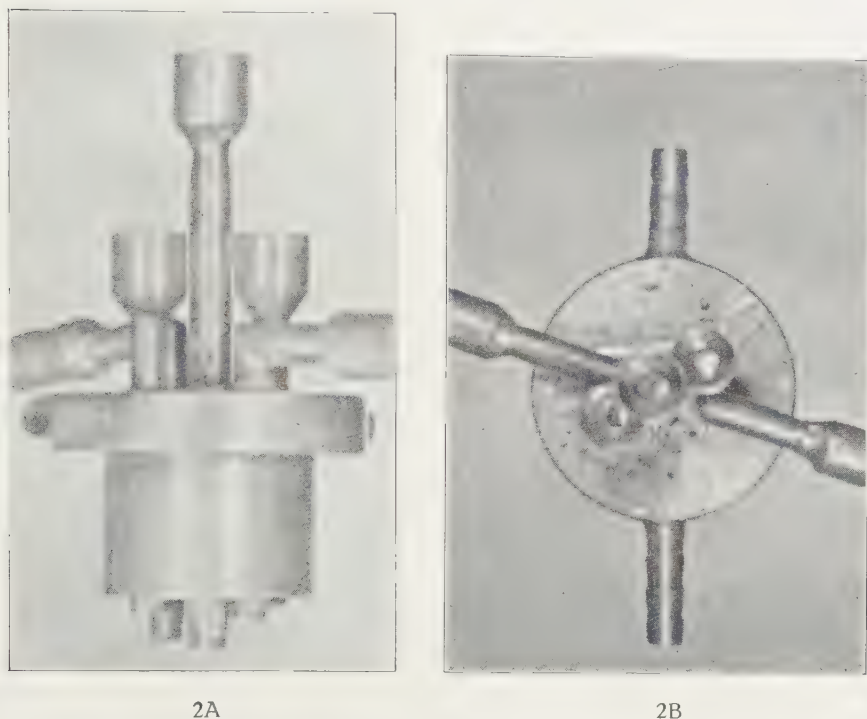


Fig. 2. To the left: The hollow Copper cylinder with its Canals of Copper and Lead and its Flange. To the right: The Cover seen from above.

moreover, even at a distance of 20 cm above the furnace, it needed intensive cooling by a rapidly streaming flow of cold water. The cylinder bore five tubes, 3 of copper and 2 of lead, — the latter being used for connecting the tube with the high-vacuum pump, whilst of the three copper tubes two oppositely arranged were used for the fixation of the copper wires bearing the wire-spiral to be investigated, whilst the third served for the purpose of a passage of the fourfold bored capillary, in the borings of which the four wires of the two thermocouples were situated. As the cover also has a flange exactly fitting to that of the hollow cylinder, a thin ring of soft rubber at both sides lightly covered with some RAMSAY-fat or better with "Apiezon" (Shell Company), was placed between the two flanges, which then were tightly pressed upon each other by means of three small, screwed claps. As to the passage of the wires of the thermocouples,

<sup>1)</sup> Originally a *soft* solder was used, but soon it became apparent that a *hard* solder had to be used, notwithstanding the greater technical difficulties of its application, because, — especially with repeated heatings, — the latter yielded longer and gave a better guarantee against leakage.



it still can be remarked, that the capillary with its fourfold borings at its upper end, — there, where it passes through the upper cover, — was over a distance of 1 cm ground off, so that the four wires lay bare; this ground part of the capillary emerged through the tube previously mentioned far enough to reach the upper, funnel-shaped enlargement of the perforation, which then was filled with molten and solidified piceine or better with "Apiezon"-glue. The hot junctions of the thermocouples were centrally placed about in the midst of the wire-spiral; the one thermocouple was connected with the horizontally recording galvanometer, the other with a sensitive pyrometer, which continuously could be read during the experiment. If the experiments are made with all necessary precautions, the vacuum-tube remains perfectly tight, notwithstanding its rather numerous inlets and outlets.

§ 4. The vacuum-tube described was heated in an electrical resistance-furnace of the type always used in this laboratory, the lower end of the tube being placed within the space of constant temperature-gradient of the furnace. In this part the increase of temperature of the furnace, when its temperature is gradually augmented, will also be most regularly distributed. In our experiments the variation of the heating current of the furnace by altering its external resistance was, up to  $600^{\circ}\text{C.}$ , completely, or at least as much as possible, avoided; in the interval of  $600^{\circ}$ — $1000^{\circ}\text{C.}$ , where often a slight supplementary regulation of the heating current by inserted external resistances proved to be necessary, the regulation was made with great precaution, in steps of 0.01 Ohm and always within stretches where no irregularities in the curve proved to occur. In the present measurements on nickel, where the temperature-interval did not exceed  $400^{\circ}$ , no supplementary regulation was needed. As to the cooling-curves, from  $1000^{\circ}$ — $600^{\circ}\text{C.}$  downwards, simply switching-off the heating circuit usually proved to be sufficiently efficient; the speed of cooling at  $1000^{\circ}\text{C.}$  then was about  $6^{\circ}$  per minute, slowly diminishing to  $3^{\circ}$  per minute at  $600^{\circ}\text{C.}$  For cooling from  $600^{\circ}\text{C.}$  downwards a slow current of air, regulated by means of a stopcock, was blown into the furnace from the lower end; in this way the speed of cooling down to  $300^{\circ}\text{C.}$  could be kept fairly constant.

§ 5. *Measurement of the Resistance of a Nickel-wire at different Temperatures between  $15^{\circ}$  and  $430^{\circ}\text{C.}$*

As a first example of measurements of this kind we here communicate the results of the application of this method to the study of the allotropic changes of *nickel*, which take place between  $350^{\circ}$  and  $380^{\circ}\text{C.}$  The measurements were made in a high vacuum as well as in an atmosphere of hydrogen under low pressure, with the purpose of studying the influence which the taking up of traces of such gases may have on the special way of transformation and on the localization of the transition-temperature itself.



The wire used (98 % Ni) had a diameter of 0.4 mm and was wound into the shape of a spiral with a length of 46.3 cm; its specific resistance (for 1000 mm length and a cross section of 1 mm<sup>2</sup>) was 0.091 Ohm at 20° C. During the measurements small thermoelectrical effects were

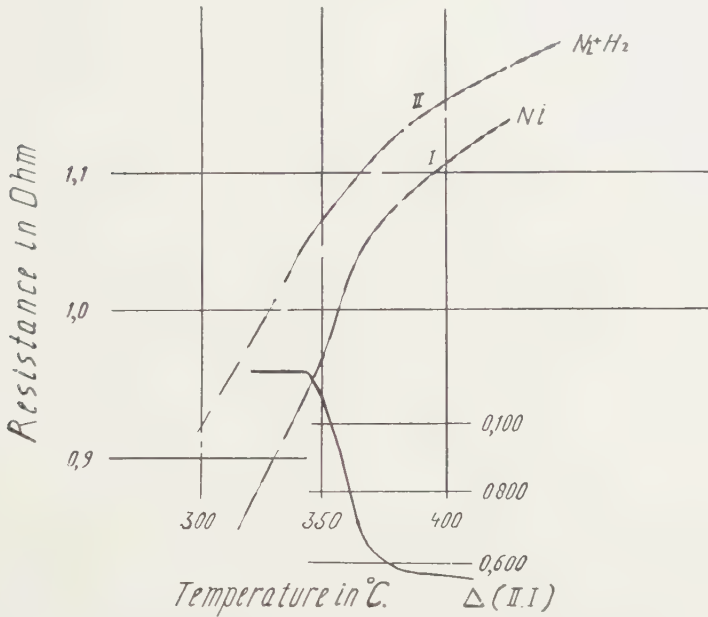


Fig. 3. The Variation of the Electrical Resistance of Nickel with the Temperature in a Vacuum and in Hydrogen.

observed, which in the final computations of the results must, of course, be eliminated. For this purpose the shift of the zero-line on the photographic plate was determined by switching off the current in the bridge and intercepting the luminous ray and then localizing the new zero-points on the photographic plate by imprinting the calibration-marks upon it at a series of temperatures below and above the transition-point under these circumstances, by a short exposure (10 sec.) of the plate to the point-shaped spot of light. Within the narrow range of temperatures of only 130°, the thermoelectrical effect is practically independent of the temperature. Several  $w$ - $t$ -curves were thus determined and, after the necessary corrections for the thermoelectrical effects and the change of resistance of the supplying conductors being duly applied, they proved to co-incide with each other within 0.1 %. As the resistance of the supplying wires leading to the WHEATSTONE-bridge also changes during the experiment, because their temperature will less or more increase, — this variation duly also has to be taken into account, although it is rather small: the total resistance of these connecting parts was 0.023 Ohm, of which 0.002 Ohm correspond to the parts within the heated tube. This correction is not yet considered here; it will be determined separately in the near future.

In Table I a review of the results obtained is given for the case that the nickel-wire was heated in a high vacuum.

Temperature $t$ in °C.:	Resistance $w$ obs. in Ohms:	Increments $\Delta$ of $w$ for every 10°.	Temperature $t$ in °C.:	Resistance $w$ obs. in Ohms:	Increments $\Delta$ of $w$ for every 10°:
320° C.	0.839		375°	1.042	
		<b>0.033</b>			$2 \times 0.010 = \mathbf{0.020}$
330	0.872	<b>0.034</b>	380	1.052	$2 \times 0.008 = \mathbf{0.016}$
340	0.906	<b>0.034</b>	385	1.060	$2 \times 0.007 = \mathbf{0.014}$
350	0.940	$2 \times 0.022 = \mathbf{0.044}$	390	1.067	<b>0.014</b>
355	0.962	$2 \times 0.027 = \mathbf{0.054}$	400	1.081	<b>0.014</b>
360	0.989	$2 \times 0.023 = \mathbf{0.046}$	410	1.095	<b>0.015</b>
365	1.012	$2 \times 0.016 = \mathbf{0.032}$	420	1.110	<b>0.014</b>
370	1.028	$2 \times 0.014 = \mathbf{0.028}$	430	1.124	

From these data it is seen that, before the first transition-point (358° C.) is reached, the increment of  $w$  per 10° C. first regularly augments to a maximum value at 358° ( $=0.054$ ), but then rapidly decreases till a constant value (0.014) is attained in the neighbourhood of 380° C., which is less than half the value observed before the allotropic changes have occurred (Curve I in Fig. 3).

Between about 350° and 365° C. the curve shows a much steeper interval: perhaps this part of the curve relates to the  $\alpha$ - + the  $\alpha'_1$ -modification (hexagonal) observed by BREDIG, which appears to be stable between 357° and 363° C.; conf. these Proceed., **34**, 818 (1931).

Now the same measurements were executed in an atmosphere of *hydrogen* of 60 mm pressure; the results obtained are recorded in Table II.

From these data it can be deduced that *nickel*, after having taken up some hydrogen on heating, has a greater resistance than the metal in vacuo, but that the temperature-coefficient of the resistance remains practically the same as before. From about 345° C. till 375° C. upwards, however, the hydrogen is gradually released: the curve  $\Delta'$  (II—I) in Fig. 3 clearly shows the course of these differences. In a stretch of transition between 345° and 375° C. there is a steep slope of the curve mentioned, the values of the ordinates rapidly decreasing to less than half the original value; whilst, on further increasing the temperature, the resistance of the still *hydrogenated nickel* slowly and gradually approaches that characteristic

TABLE II.  
The Variation of the Electrical Resistance  $w$  of a Nickel-wire when heated in  
Hydrogen ( $p = 60$  m.m.) at Temperatures between  $300^\circ$  and  $430^\circ$  C.

Temperature $t$ in $^\circ\text{C}.$ :	Resistance $w$ obs. in Ohms:	Increments $\Delta$ of $w$ for every $10^\circ$ :	Temperature $t$ in $^\circ\text{C}.$ :	Resistance $w$ obs in Ohms:	Increments $\Delta$ of $w$ for every $10^\circ$ :
$300^\circ$ C.	0.894		$370^\circ$ C.	1.091	
310	0.924	<b>0.030</b>	375	1.102	$2 \times 0.011 = \mathbf{0.022}$
320	0.954	<b>0.030</b>	380	1.110	$2 \times 0.008 = \mathbf{0.016}$
330	0.986	<b>0.032</b>	385	1.117	$2 \times 0.007 = \mathbf{0.014}$
340	1.022	<b>0.036</b>	390	1.124	$2 \times 0.007 = \mathbf{0.014}$
350	1.047	<b>0.025</b>	400	1.136	<b>0.012</b>
355	1.059	$2 \times 0.012 = \mathbf{0.024}$	410	1.148	<b>0.012</b>
360	1.072	$2 \times 0.013 = \mathbf{0.026}$	420	1.159	<b>0.011</b>
365	1.081	$2 \times 0.009 = \mathbf{0.018}$	430	1.170	<b>0.011</b>
		$2 \times 0.010 = \mathbf{0.020}$			

of the pure metal. The first steep slope of this part is most probably connected with the insertion of the hexagonal  $\alpha'$ -form between the  $\alpha$ - and  $\beta$ -modifications.

The Differences $\Delta'$ between Curves II and I between $320^\circ$ and $430^\circ$ C.			
$t$ :	$\Delta'$ :	$t'$ :	$\Delta'$ :
$320^\circ$	0.115	$375^\circ$	0.060
330	0.114	380	0.058
340	0.116	385	0.057
350	0.107	390	0.057
355	0.097	400	0.055
360	0.083	410	0.053
365	0.069	420	0.049
370	0.063	430	0.046

We soon intend to publish more results of this kind: the case here studied may, for the moment, be sufficient to demonstrate the applicability of the method described.

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**Chemistry.** — *On the Preparation and Properties of Some Ortho-Diamino-Cyclohexanes.* By F. M. JAEGER and J. A. VAN DIJK.

(Communicated at the meeting of February 29, 1936).

§ 1. For the purpose of continuing our investigations<sup>1)</sup> about the influence which the introduction of bivalent and optically-active diamines into the complex ions of bi- and polyvalent metals has on the molecular rotations and rotatory dispersion of the antipodes, it was necessary to prepare a number of cyclic diamino-compounds suited for this kind of research. As the formation of complex ions of this type occurs more easily with 1-2-, than with 1-3- or 1-4-diamines, it was beforehand indicated to limit our tentatives to the preparation of *ortho*-substituted *diamino*-derivatives of *cyclohexane*. For this reason we started the synthesis of 1-2-*Diaminocyclohexane*, 1-*Methyl-2-3-* and 1-*Methyl-3-4-diamino-cyclohexanes* and of 3-4-*Diamino-p-menthane* (= 1-*Methyl-4-isopropyl-3-4-diamino-cyclohexane*). In this paper some data about the results obtained and of some of the properties of the bases mentioned are given; later on their full description and that of the complex salts derived from them will be published in detail.

The general way followed in the synthesis of the bases of the first group mentioned was: *Cyclohexanone* → *Cyclohexanone-oxalylic ester* → *Cyclohexanone-carboxylic-ester* → *Cyclohexanone-isonitrosocompound* (= *-mon-oxime*) → *Cyclohexane-dioxime* → *Diamino-cyclohexane*. The last mentioned base of the series was prepared, starting from *Menthone* → *Nitro-menthone* → *Aminomenthone* → *Aminomenthone-oxime* → *Diamino-menthane*, in the way followed by KONOWALOW and ISCHEWSKI<sup>2)</sup> but somewhat modified, so as to ascertain a better yield of the product.

§ 2. As an example of the general way of preparation of the three bases first mentioned, the synthesis of 1-*methyl-2-3-diaminocyclohexane* will here be described more particularly; the preparation of the other bases of this series occurs in a completely analogous way.

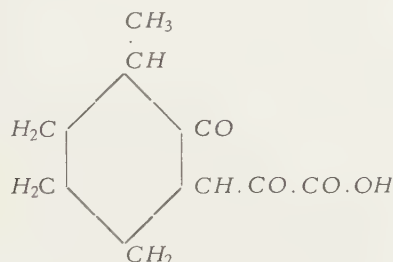
200 Grammes of 1-*methyl-2-cyclohexanone* (boilingpoint: 164°—165° C.) and 300 grammes of *diethyloxalate* (boilingpoint: 186° C.) are mixed and thoroughly cooled at —15° C. The mixed liquids are, under perpetual stirring, slowly added to an equally cooled, freshly prepared

<sup>1)</sup> F. M. JAEGER and H. BLUMENDAL, *Zeitschr. f. anorg. Chem.*, **175**, 161 (1928).

<sup>2)</sup> M. KONOWALOW and W. ISCHEWSKI, *Ber. d. d. chem. Ges.*, **31**, 1478 (1898); cf also: *ibidem*, **28**, 1054 (1895).



solution of 40 grammes sodium in 650 grammes of absolute ethylalcohol<sup>1)</sup>, which is contained in a reservoir of about 4 liters volume. Under continuous stirring the whole quantity is added in 1 or 2 hours; the contents of the vessel now were changed into a thick, pale yellow mass, which still for some time afterwards is stirred under cooling and then is left standing at room-temperature for 24 hours. The yellow mass now is poured into about 4.5 liters of a cooled 30 % solution of somewhat more than the calculated quantity of sulphuric acid. A reddish or yellow oily liquid is separated from the acid solution, collected, washed and treated with a solution of sodium bicarbonate, whilst the aqueous solution is three or four times extracted with ether, the latter distilled off and the residue added to the first mass; then so much ether is added to it, that a clear reddish solution is obtained. This is dried with anhydrous sodium sulphate and the dried ethereal solution left standing at room-temperature till all ether is evaporated. Besides the liquid condensation product, ordinarily some solid substance is obtained, which proves to be the free *oxalylic* acid:



which crystallizes from water in beautiful, colourless, monoclinic crystals with the axial ratio:  $a : b : c = 1.712 : 1 : 1.724$ ;  $\beta = 73^\circ 26'$  and the forms:  $r = \{101\}$ , often predominant;  $c = \{001\}$  broad, sometimes predominant;  $m = \{110\}$ , well developed;  $s = \{201\}$ , narrow, like  $b = \{010\}$ ; sometimes  $\omega = \{211\}$  as a very narrow truncation of the edges  $r : m$ . (Fig. 1).

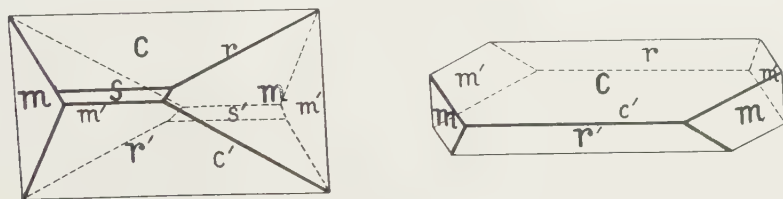


Fig. 1. 1-Methyl- 2-Cyclohexanone- 3-Oxalylic Acid.

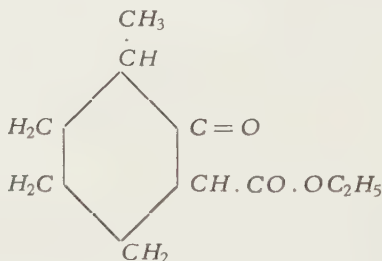
Often the edges of the crystals are rounded;  $s$  and  $b$  usually yield only weak reflections, the other faces very good ones. The habitus of the crystals is represented in Fig. 1.

<sup>1)</sup> A. KÖTZ and L. HESSE, Ann. d. Chemie, 342, 315 (1905).

Angular Values:	Observed:	Calculated:
$c : m = (001) : (110) =^* 81^\circ 28'$		—
$m : r = (110) : (10\bar{1}) =^* 63$	43	—
$c : r = (001) : (\bar{1}01) =^* 74$	50	—
$c : s = (001) : (201) = 50$	39	$50^\circ 48'$
$s : r = (201) : (10\bar{1}) = 54$	31	54 22
$b : m = (010) : (110) = 31$	28	31 22
$m : m = (110) : (110) = 62$	56	62 44

No distinct cleavability was observed.

The impure condensation product is subjected to a vacuum distillation and the fraction boiling under a pressure of 12—13 mm at  $97^\circ\text{C}$ . or lower, — which chiefly consists of water, unchanged methylcyclohexanone and diethyloxalate, — separately collected. During this distillation a partial decomposition of the oxalylic ester formed already takes place under development of carbon monoxide; the remaining liquid is, in order to complete this decomposition, during a sufficiently long time heated on a sand-bath in a flask with reflux-cooler at  $210^\circ\text{—}220^\circ\text{C}$ ., till no carbon monoxide is any longer set free. The *carboxylic ester* thus generated:



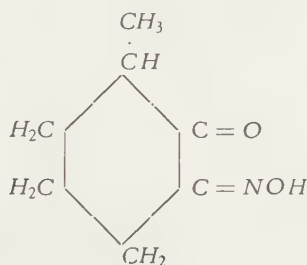
is now subjected to a vacuum distillation and the fraction boiling under 12—13 mm at  $115^\circ\text{—}116^\circ.5\text{C}$ . collected. The yield of this pure ester never exceeds 62 % of the calculated quantity, but occasionally is less than this (42 %): from 1530 grammes methylcyclohexanone we obtained about 1050 grammes of the carboxylic ester (45 %—46 %); in the vessel remains a dark, resinous mass, whilst a small quantity of oxalylic acid and a good deal of unchanged diethyloxalate, some water, alcohol and other by-products are simultaneously obtained. It proved advisable to subject no more than about 200 grammes of methylcyclohexanone at the same time to this condensation, as with greater quantities the final yield seems to decrease.

§ 3. The pure carboxylic ester thus obtained now is mixed with somewhat more than the calculated quantity of a 6 % solution of potassium hydroxide and the theoretical quantity of sodium nitrite and during 48 hours shaken at room-temperature in a hermetically closed bottle<sup>1)</sup>.

<sup>1)</sup> E. TAKENS, Diss. Göttingen, 30 (1910).

After the liquid is poured into a cooled 30 % -solution of sulphuric acid, the solid white *isonitroso*-compound is precipitated, which is filtered off, whilst from the solution, when extracted with ether, still somewhat of another monoxime, besides a coloured liquid, is obtained; the latter is a mixture of both *isonitroso*-compounds. The first mentioned monoxime readily crystallizes from methyl- or ethylalcohol, still better from ethylacetate, in beautiful, colourless flat crystals, which, under decomposition, melt at 167° C. From 1050 grammes of the carboxylic ester we, in this way, obtained 500 grammes of the solid monoxime, 14 grammes of the other monoxime melting at 65° C. and 140 grammes of the liquid mixture of the two compounds.

1-Methyl-2-Oxo-3-Isonitroso-cyclohexane (mpt. : 167° C.) of the composition:



crystallizes from alcohol or ethylacetate in parallelogram-shaped, colour-

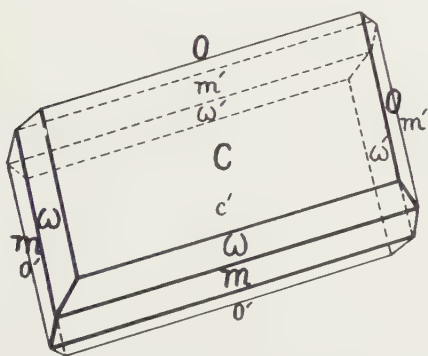


Fig. 2. 1-Methyl- 2-Oxo-3-Isonitroso-Cyclohexane

less, monoclinic tables. They are monoclinic-prismatic, with the axial ratio:  $a : b : c = 1.933 : 1 : 1.223$  and  $\beta = 73^\circ 16'$ . The perfectly transparent crystals (Fig. 2) show the following forms:  $c = \{001\}$ , very lustrous and predominant;  $m = \{110\}$ ,  $o = \{111\}$  and  $\omega = \{111\}$  about equally broad and all yielding very good reflections. Sometimes  $o$  is absent. The form  $b = \{010\}$  is only small, giving weak images. The crystals are flat tables parallel to  $\{001\}$ .

Angular Values:	Observed:	Calculated:
$c : \omega = (001) : (111) = ^* 48^\circ 7'$		—
$\omega : m = (111) : (110) = ^* 34 \quad 1$		—
$m : m = (110) : (1\bar{1}0) = ^* 123 \quad 14$		—
$c : m = (001) : (110) =$	82   8	$82^\circ 8'$
$c : o = (001) : (111) =$	57   51	58   11

<i>Angular Values:</i>	<i>Observed:</i>	<i>Calculated:</i>
$m : b = (110) : (010) =$	28 23	28 23
$\omega : \omega = (111) : (111) =$	83 4	82 48
$\omega : b = (111) : (010) =$	48 33	48 36
$m : o = (110) : (\bar{1}\bar{1}) =$	40 1	39 42

Cleavable parallel to  $\{001\}$ .

The plane of the optical axes is  $\{010\}$ . The apparent axial angle on  $\{001\}$  is fairly great.

*Reactions of the Monoxime.* An alcoholic solution of this compound, if added to aqueous solutions of the following salts, yields:

- 1) with *ferrous sulphate* a beautifully reddish-violet solution.
- 2) with *ferric chloride* a dark violet, almost black solution; on heating, its colour changes into a reddish-brown.
- 3) with *copper sulphate* a yellowish-green solution, the colour turning to a brownish-green on heating the liquid.
- 4) with *nickel sulphate* no change of the colour of the solution occurs, but on heating it turns to a more yellowish-green, and finally a dull red, complex nickel salt is precipitated.
- 5) with *cobaltous chloride* a brick-red solution is obtained, its colour getting darker on heating the liquid.
- 6) with *sodium rhodium chloride* no appreciable change of colour; but on heating the latter turns to a yellow-orange.

§ 4. As to the isomeric monoxime formed in small quantity and melting at  $65^{\circ}$  C., it can be remarked that its reactions with the reagents mentioned above differ only slightly, but yet distinctly, from those of the monoxime of meltingpoint  $167^{\circ}$  C.: thus *ferrous sulphate* in the cold yields about the same violet colour, which on heating, however, gets much darker; *ferric chloride* gives a violet-blue solution which on heating turns to a pale brown colour; *copper sulphate* gives about the same coloration as before, but on heating this turns to a dark emerald-green. The principal difference, however, between the two monoximes manifests itself by the different colours of the precipitate formed, if an aqueous solution of a *nickel* salt and some hydroxylamine is heated with them: the thus formed *dioxime* in the first case yields a clear *red*, in the second case an *orange*-coloured internally complex *nickel* salt, proving that the two dioximes formed are distinctly different from each other. To this difference we will return later on in describing the dioximes themselves.

Finally the viscous liquid extracted from the aqueous solution by means of ether (see above), evidently being a mixture of the two monoximes, — as is proved by the fact that, on standing, the monoxime of meltingpoint  $167^{\circ}$  C. is gradually crystallizing from it, — yields reactions which are

intermediate between those described in the two cases, besides those of the *dioxime*, as is proved by the *orange-red* precipitate with *nickel sulphate* and the colorations with *ferric chloride* and *copper sulphate*. Evidently a minute quantity of the corresponding dioximes is also present in it, although it is not clear, how they can have been formed in the process. Tentatives made with the purpose of distilling the liquid in vacuo remained without result, as the substance evidently decomposes. On treating it with hydroxylamine (see § 5), no crystallized product could be obtained, although, on reduction, it chiefly gave the same *diamino-cyclohexane* as the pure dioxime derived from the monoxime of meltingpoint  $167^{\circ}\text{C.}$ , — besides a monobasic substance, which most probably is an amino-methyl-cyclohexane (see § 6).

§ 5. The solid monoxime of meltingpoint  $167^{\circ}\text{C.}$ , after careful purification by recrystallizing it from ethylacetate, was transformed into the corresponding *dioxime* in the following way<sup>1)</sup>: 10 grammes of the monoxime were dissolved in methylalcohol and then added to a methylalcoholic solution of 6 grammes hydroxylamine-hydrochloride + of 1.98 grammes sodium dissolved in  $25\text{ cm}^3$  methylalcohol. The mixture was left standing for 24 hours at room-temperature, the sodiumchloride filtered off and the alcohol distilled off in vacuo at  $40^{\circ}\text{C.}$  The *dioxime* which was obtained in a yield of 96 %—100 % of the calculated quantity was repeatedly recrystallized from alcohol or ethylacetate or from a mixture of hot water and alcohol: it crystallizes in colourless small needles with the same meltingpoint as the monoxime, i.e.  $167^{\circ}\text{C.}$  Although it seems to be identical with the dioxime obtained by WALLACH and WEISENBORN<sup>2)</sup> in quite another way, there are some striking discrepancies between their description of the compound and ours: not only did we never meet with the difficulties in reducing the substance to the diamino-compound mentioned by them, but most remarkable is that, notwithstanding the identity of the meltingpoint with that of our preparation, they describe the colour of the complex *nickel salt* as being *orange-red*, whilst we always found a *pure red* colour and an *orange* colour only with the nickel salt of the isomeric dioxime of meltingpoint  $65^{\circ}\text{C.}$ , which in our synthesis was obtained as a by-product only in a small amount. The *dioxime* obtained from this monoxime of meltingpoint  $65^{\circ}\text{C.}$  crystallizes from alcohol in yellowish, not perfectly pure crystals which melt at  $140^{\circ}\text{C.}$  It is possible that the two monoximes ( $65^{\circ}$  and  $167^{\circ}\text{C.}$ ), as well as the two corresponding dioximes ( $140^{\circ}$  and  $167^{\circ}\text{C.}$ ) are related to each other as *syn*- and *anti*-isomerides. Most probably the preparation of the German authors has been a mixture of the two dioximes, as may be deduced from their indication of the colour of their complex *nickel salt*.

<sup>1)</sup> E. TAKENS, loco cit., 45.

<sup>2)</sup> O. WALLACH and A. WEISENBORN, Lieb. Ann. **437**, 148 (1924).



The *dioxime* obtained yielded the following reactions:

- 1) with *ferrous sulphate* it gave an orange-brown solution and finally a precipitate, getting darker on heating.
- 2) with *ferric chloride* a brown solution was obtained, which, on heating, became darker brown.
- 3) with *copper sulphate* the solution got an olive-green colour.
- 4) with *nickel sulphate* immediately an insoluble, red precipitate of the internal complex nickel salt is produced, which is decomposed by hydrochloric acid, so that the solution again turns green.
- 5) with *cobaltous chloride* an insoluble, dark red precipitate is formed, which dissolves in hydrochloric acid to a blue solution.
- 6) with *sodium rhodium chloride* an orange-red solution is obtained, which does not change on heating.

§ 6. The *dioxime* can be quantitatively reduced to the *diamino-compound* in portions of 10 grammes by means of an excess of sodium in boiling absolute alcohol. To this end the fivefold of the calculated quantity of sodium is given into a wide, round-bottom flask provided with a reflux-cooler and then a small quantity of ethylalcohol is added. The alcoholic solution of the *dioxime* now is rapidly added from a dropping funnel, whilst the content of the flask is continuously stirred; successively more alcohol is then added. When all *dioxime* and the necessary quantity of alcohol is added, the mixture is for some hours heated on the water bath, till all the sodium is completely dissolved. Then the reaction product is distilled with water vapour and the volatile base caught in dilute hydrochloric acid; it is advisable to avoid a great excess of the acid. The solution is finally evaporated on the water bath to a small volume, the liquid discoloured with coal, filtered and left to crystallization over sulphuric acid in an exsiccator. The *hydrochloride* crystallizes as a mass of fine, colourless needles, which contain 13.28  $H_2O$  and on analysis yield: 12.12 % *N* and 30.71 % *Cl*; so that its constitution is:  $C_7H_{16}N_2, HCl + 2H_2O$ .

For the isolation of the free base a concentrated solution of this salt, from a dropping bottle, is slowly added to an excess of solid potassium hydroxide, contained in a vessel provided with a cooler; the flask is continuously cooled by means of ice and salt. The liquid base thus obtained is preserved for a long time over solid potassium hydroxide, then equally over metallic sodium and finally distilled in vacuo over fresh sodium in an apparatus provided with glass-joints; as the base rapidly attracts water vapour and carbon dioxide, it is necessary to provide all recipients with tubes filled with sodium hydroxide and calcium chloride. The pure base boils at  $84^\circ C$ . under 12 mm pressure; it is a colourless, strongly alkaline liquid, which has an odour reminding of ethylenediamine, and like this, attracts the carbon dioxide of the air with great avidity and readily condenses water vapours on it.

On reducing the dioxime obtained from the oily monoxime, the same bivalent base was obtained; but besides it another colourless and much more volatile basic liquid, which constantly boiled at  $41^{\circ}\text{C}$ . under 12 mm pressure. It has a penetrating amine-like odour, is only *monobasic*, precipitates the hydroxides of iron and nickel from the aqueous solutions of their salts and most probably is an *amino-methyl-cyclohexane*. Its tendency to form complex metallic salts is much less than that of the diamines. The base contains 12.25 % N; calculated for *amino-methylcyclohexane*: 12.39 % N.

Its *benzoyl*-derivative had a meltingpoint of  $106^{\circ}\text{C}$ .; so that the base must be the *1-methyl-3-amino-cyclohexane*, as the *benzoyl*-derivatives of the 1-2-, and of the 1-4-isomerides melt at  $147^{\circ}$  and  $180^{\circ}\text{C}$ . respectively. The amino-compound is only sparsely soluble in water; its hydrochloride melts under decomposition at  $260^{\circ}$ — $265^{\circ}\text{C}$ .

Of the dioxime of meltingpoint  $65^{\circ}\text{C}$ . finally too little was left for reduction-experiments, so that it is not yet possible to say, what is the corresponding diamine in this case. In the distillation of the bulk of the crude base we got, however, a small fraction which constantly distilled between  $79^{\circ}$  and  $80^{\circ}\text{C}$ . under 12 mm pressure, i.e.  $4^{\circ}$  lower than the base already described.

*1-Methyl-2-3-diamino-cyclohexane* forms with a number of metallic salts complex compounds of various types, which also will be described in detail in a later publication.

§ 7. In the same way the correspondent bivalent bases derived from *cyclohexanone* and from *1-Methyl-3-* and *1-Methyl-4-cyclohexanone* were prepared and some of their properties studied.

*Cyclohexanone* (boilingpoint:  $155^{\circ}\text{C}$ .) yielded a *carboxylic ester* which under 14 mm pressure boils at  $111^{\circ}$ — $112^{\circ}\text{C}$ ., under 11—12 mm at  $106^{\circ}$ — $107^{\circ}\text{C}$ . As a by-product in its synthesis a little of the corresponding *oxalylic acid*<sup>1)</sup> (meltingpoint:  $122^{\circ}\text{C}$ .) was obtained in well measurable crystals (Fig. 3), which are rhombic-bipyramidal with the axial ratio:  $a : b : c = 1.402 : 1 : 1.553$  and the forms:  $a = \{100\}$ , predominant;

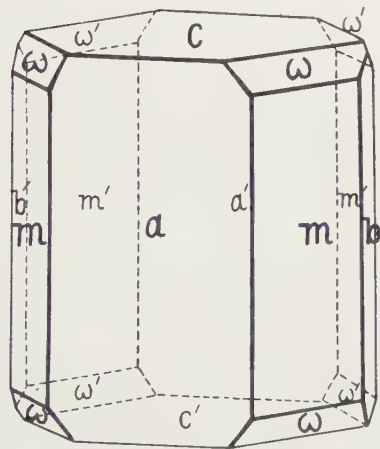


Fig. 3. *Cyclohexanone-oxalylic Acid*.

$c = \{001\}$ , well developed, like  $m = \{110\}$ ;  $r = \{201\}$  and  $b = \{010\}$ , narrow;  $\omega = \{111\}$ , small, but very lustrous. The crystals are tabular parallel to  $\{100\}$ .

<sup>1)</sup> A. KÖTZ and A. MICHELS, Lieb. Ann. d. Chem., 350, 211 (1906).

<i>Angular Values:</i>	<i>Observed:</i>	<i>Calculated:</i>
$a : m = (100) : (110) =^* 54^\circ 30'$	—	—
$c : \omega = (001) : (111) =^* 62 \quad 20$	—	—
$m : b = (110) : (010) = 35 \quad 30$	35° 30'	35° 30'
$\omega : m = (111) : (110) = 27 \quad 40$	27 40	27 40
$a : \omega = (100) : (111) = 58 \quad 58$	59 3	59 3
$\omega : m = (111) : (\bar{1}10) = 73 \quad 3$	73 15	73 15
$\omega : b = (111) : (010) = 43 \quad 53$	43 51	43 51
$c : r = (001) : (201) = 65 \quad 30$	65 42	65 42
$r : a = (201) : (100) = 24 \quad 30$	24 18	24 18

No distinct cleavability was observed.

The optical extinction on *a* is normal; most probably the *a*-axis is the second bisectrix, but the axial image was not very distinct.

From the carboxylic ester mentioned the *isonitroso*-compound was prepared in the way described: it is a non-crystallizable, oily liquid. The *dioxime*, however, is well crystallized and melts at 187°—189° C. On reduction with sodium and alcohol, the *diamino-cyclohexane* is obtained, besides a lower boiling monobasic substance. *Diamino-cyclohexane* boils at 79°—81° C. under a pressure of 15 mm. It is a colourless, strongly alkaline liquid, which readily absorbs the carbon dioxide of the air and condenses water-vapours upon itself. It possesses the *trans*-configuration, as is proved by its *resolvability into optical antipodes*. The base forms typical complex salts; thus, with *cobaltous chloride* and after oxidation with hydrogen peroxide, a green *praseo*- and an orange-brown *triammino*-salt.

As already mentioned, also in this case a fraction was obtained of the lower boilingpoint 37°—39° C. under 16 mm pressure. It is a colourless, alkaline liquid, which proved to be monobasic and the nitrogen-content of which was found at 13.86 %; evidently it is, therefore, the *amino-cyclohexane* (14.1 % N). This was finally proved<sup>1)</sup> (BIJKERK) by means of its boilingpoint at ordinary pressure: 134°—135° C. and by the meltingpoint of its pure hydrochloride, which was determined to be 206°—207° C.

1-*Methyl-3-cyclohexanone* (boilingpoint: 169° C.) gives a *carboxylic ester*, — in a yield of 60—62 % of the calculated quantity, — which under 13 mm pressure boils at 118°—120° C. Its *monoxime* is a colourless, crystallized substance (meltingpoint: 159° C.), which can readily be transformed into the crystallized *dioxime* (meltingpoint: 180°—181° C.); the latter is identical with the *dioxime* finally obtained from 1-*methyl-4-cyclohexanone*. With *nickel* salts it forms a beautifully red complex salt.

<sup>1)</sup> A. BAEYER, Ann. d. Chem., **278**, 103 (1894); W. MARKOWNIKOFF, *ibid.*, **302**, 22 (1898).

The dioxime was reduced to the *diamino-cyclohexane* in the way previously mentioned; 1-methyl-3-4-diamino-cyclohexane is a colourless, strong alkaline liquid, which under a pressure of 13 mm boils at 81°.5 C.

It readily combines with the carbon dioxide of the air and condenses water vapours upon itself.

1-Methyl-4-cyclohexanone (boilingpoint: 169° C.) gives a *carboxylic ester*, in a yield of 55—60 % of the calculated quantity; the ester boils at 113°—115° C. under a pressure of 13 mm. The corresponding *isonitroso-compound (monoxime)* is a non-crystallizable liquid; the *dioxime* (melting-point: 180°—181° C.), however, is solid and identical with that obtained from 1-methyl-3-cyclohexanone. Both dioximes in consequence on reduction yield the same diamino-compound of boilingpoint: 81°.5 C. under 13 mm pressure.

With *cobaltous chloride* this *diamino-cyclohexane*, on simultaneous oxidation with hydrogen peroxide, furnishes a beautiful, green *praseo-salt*; with *nickel-* and *copper sulphate* violet complex salts are formed.

§ 8. Finally 3-4-diamino-menthane was prepared, starting from *menthone*. This compound was first transformed into the liquid *nitro-menthone*; the crude substance ordinarily still contains 30 % *menthone*. It was reduced to *amino-menthone* (boilingpoint: 215° C. under 16 mm pressure) by heating it with tin and hydrochloric acid on the water-bath. The yield is appreciably improved by the addition of alcohol to the reduction-mixture and boiling at a reflux-cooler for a considerable time; if the unchanged *menthone* present is accounted for, a yield of 70 % in this reaction may be attained. This *amino-menthone* then was transformed into the corresponding *oxime* by means of hydroxylamine; *amino-menthone-oxime* is a liquid boiling at 182° C. under 16 mm pressure. By reduction with sodium and boiling alcohol in the way described, the compound was transformed into the theoretical quantity of *diamino-menthane*, a colourless, strongly alkaline base, which under 12 mm pressure boils at 110°—113° C. It readily combines with water vapours and carbon dioxide of the air; with metal salts it forms complex compounds; i.e. with *cobaltous chloride*, — on simultaneous oxidation with  $H_2O_2$ , — a beautiful, green *praseo-salt* and also typical complex *nickel-* and *copper* salts.

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**Mathematics.** — *Einige Integraldarstellungen aus der Theorie der BESSELSchen und WHITTAKERSchen Funktionen.* (Erste Mitteilung).  
Von C. S. MEIJER. (Communicated by Prof. J. G. VAN DER CORPUT).

(Communicated at the meeting of February 29, 1936).

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# Einleitung.

Es bezeichnen  $H_\nu^{(1)}(z)$  und  $H_\nu^{(2)}(z)$  die beiden HANKELschen Funktionen. Es sei ferner  $J_\nu(z)$  die gewöhnliche BESSELSche Funktion,  $W_{k,m}(z)$  die WHITTAKERSche Funktion <sup>1)</sup> und

$${}_rF_s(a_1, \dots, a_r; b_1, \dots, b_s; z)$$

die verallgemeinerte hypergeometrische Funktion.

Es bezeichnen weiter  $P_n^m(z)$  und  $Q_n^m(z)$  die zugeordneten LEGENDRESchen Funktionen erster und zweiter Art <sup>2)</sup>.

Ueberdies setze ich noch

$$K_\nu(z) = \frac{1}{2} \pi i e^{\frac{1}{2} \nu \pi i} H_\nu^{(1)}(z e^{\frac{1}{2} \pi i}),$$

$$I_\nu(z) = e^{-\frac{1}{2} \nu \pi i} J_\nu(z e^{\frac{1}{2} \pi i})$$

und

$$\mathbf{L}_\nu(z) = \left(\frac{1}{2} z\right)^{\nu+1} \sum_{m=0}^{\infty} 2^{2m} I'(\frac{\nu}{2} + m) I'(\frac{\nu}{2} + \nu + m) z^{2m}$$

Es sei ferner <sup>4)</sup>

$$\left. \begin{aligned} \psi_{p,q} \left( \zeta \left| \begin{array}{c} c_1, \dots, c_{p+2} \\ b_1, \dots, b_{p+2} \end{array} \right. \right) &= \\ &= \sum_{j=1}^q \frac{\prod_{h=1}^q \Gamma(c_j - c_h) \prod_{h=1}^{p-q+3} \Gamma(1 - c_j + b_h)}{\prod_{h=q+1}^{p+2} \Gamma(1 - c_j + c_h) \prod_{h=p-q+4}^{p+2} \Gamma(c_j - b_h)} \zeta^{1-c_j} \times \\ &\times {}_{p+2}F_{p+1}(1 - c_j + b_1, \dots, 1 - c_j + b_{p+2}; 1 - c_j + c_1, \dots, 1 - c_j + c_{p+2}; -\zeta). \end{aligned} \right\} \quad (1)$$

1) Für die Definition von  $W_{k,m}(z)$  siehe man WHITTAKER and WATSON, [17], chapter XVI; siehe auch MEIJER, [11]. (Die fett gedruckten Zahlen beziehen sich auf das Literaturverzeichnis).

2) Für die Definition der Funktionen  $P_n^m(z)$  und  $Q_n^m(z)$  vergl. man BARNES, [5] und HOBSON [9] und [10]. BARNES und HOBSON benutzen eine verschiedene Bezeichnung für  $Q_n^m(z)$ . Man hat nämlich

$$\{Q_n^m(z)\}_H = \frac{e^{m\pi i} \sin n\pi}{\sin(n+m)\pi} \{Q_n^m(z)\}_B,$$

wo  $\{Q_n^m(z)\}_H$  die Definition von HOBSON und  $\{Q_n^m(z)\}_B$  die Definition von BARNES bedeutet; siehe BARNES, [5], S. 100 und HOBSON, [10], S. 196. In der vorliegenden Abhandlung ist stets

$$Q_n^m(z) = \{Q_n^m(z)\}_H.$$

$$3) \quad \mathbf{L}_\nu(z) = e^{-\frac{1}{2}(\nu+1)\pi i} \mathbf{H}_\nu(z e^{\frac{1}{2}\pi i}),$$

wo  $\mathbf{H}_\nu(z)$  die STRIVESche Funktion bezeichnet. Man vergl. WATSON, [16], S. 329.

4) Ein leeres Produkt wird gleich 1 gesetzt. Der Stern bedeutet, dass die Zahl  $1 - c_j + c_j$  in der Reihe  $1 - c_j + c_1, \dots, 1 - c_j + c_{p+2}$  nicht vorkommt.

Ich nehme hierbei an, dass  $\zeta \neq 0$ ,

$$0 \leq p, \quad 1 \leq q \leq p+2, \quad \dots \quad (2)$$

$$c_j - c_h \text{ nicht ganz } (j=1, \dots, q; h=1, \dots, q; j \neq h) \quad \dots \quad (3)$$

und

$$c_j - b_h \neq 1, 2, 3, \dots \quad (j=1, \dots, q; h=1, \dots, p-q+3) \quad \dots \quad (4)$$

ist <sup>5)</sup>. Schliesslich setze ich

$$\left. \begin{aligned} B_{p,r} \left( w \left| \begin{array}{c} a_1, \dots, a_p \\ b_1, \dots, b_{p+2} \end{array} \right. \right) = \\ = \sum_{h=1}^{r+2} \frac{\prod_{j=1}^{p-r} \Gamma(1+b_h-a_j) \prod_{\substack{j=1 \\ j \neq h}}^{r+2} \Gamma(b_j-b_h)}{\prod_{j=p-r+1}^p \Gamma(a_j-b_h) \prod_{j=r+3}^{p+2} \Gamma(1+b_h-b_j)} w^{b_h} \times \\ \times {}_pF_{p+1}(1+b_h-a_1, \dots, 1+b_h-a_p; 1+b_h-b_1, \dots, 1+b_h-b_{p+2}; w). \end{aligned} \right\} \quad (5)$$

Hierin wird  $w \neq 0$ ,  $0 \leq r \leq p$ ,

$$a_j - b_h \neq 1, 2, 3, \dots \quad (j=1, \dots, p-r; h=1, \dots, r+2)$$

und

$$b_j - b_h \text{ nicht ganz } (j=1, \dots, r+2; h=1, \dots, r+2; j \neq h)$$

vorausgesetzt.

In der vorliegenden Arbeit werde ich unter Annahme der obigen Bezeichnungen den folgenden Satz beweisen <sup>6)</sup>:

**Satz. Voraussetzungen:** 1. Es sei

$$w \neq 0, \quad -\pi < \arg w < \pi.$$

2. Es seien  $p$  und  $r$  ganz mit

$$0 \leq r \leq p. \quad \dots \quad (6)$$

<sup>5)</sup> Falls  $c_j - c_h = 1, 2, 3, \dots$  ( $j=1, \dots, q; h=q+1, \dots, p+2$ ) ist, bekommt die rechte Seite von (1) einen Sinn durch einen Grenzübergang. Denn es gilt z.B. (auch für  $p=0, -1, -2, \dots$ )

$$\frac{1}{\Gamma(\beta)} {}_3F_2(a, b, c; \alpha, \beta; z) = \frac{1}{\Gamma(\beta)} + \frac{abcz}{\alpha \Gamma(\beta+1)} + \dots$$

Formel (40) von § 2 gibt die analytische Fortsetzung von  $\Psi_{p,q}(z)$  für  $|z| > 1$ .

<sup>6)</sup> Verwandte Sätze kommen vor in meinen Arbeiten [12], [13] und [14].

3. Es genügen die Zahlen  $a_1, \dots, a_p$  und  $b_1, \dots, b_{p+2}$  den Bedingungen

$$a_j - a_h \text{ nicht ganz } (j = 1, \dots, p-r; h = 1, \dots, p-r; j \neq h), \quad (7)$$

$$a_j - b_h \neq 1, 2, 3, \dots (j = 1, \dots, p-r; h = 1, \dots, r+2), \quad (8)$$

$$b_j - b_h \text{ nicht ganz } (j = 1, \dots, r+2; h = 1, \dots, r+2; j \neq h). \quad (9)$$

Behauptung:

$$\left. \begin{aligned} B_{p,r} \left( w \left| \begin{array}{c} a_1, \dots, a_p \\ b_1, \dots, b_{p+2} \end{array} \right. \right) = \\ = 2 \int_0^\infty u^{\beta-\alpha} J_{\alpha+\beta-1}(2u) \Psi_{p,p-r+1} \left( \frac{u^2}{w} \left| \begin{array}{c} 1-\alpha, a_1, \dots, a_p, \beta \\ b_1, \dots, b_{p+2} \end{array} \right. \right) du. \end{aligned} \right\} \quad (10)$$

Hierin sind  $\alpha$  und  $\beta$  beliebige Zahlen mit <sup>7)</sup>

$$\Re(\alpha - \beta + 2b_j) > -\frac{1}{2} \quad (j = 1, \dots, r+2), \quad (11)$$

$$\Re(\alpha + \beta) > 0, \quad (12)$$

$$\Re(\beta - a_j) > -1 \quad (j = 1, \dots, p-r), \quad (13)$$

$$\alpha + a_j \text{ nicht ganz } (j = 1, \dots, p-r), \quad (14)$$

$$\alpha + b_j \neq 0 \quad (j = 1, \dots, r+2). \quad (15)$$

Die Funktion  $B_{p,r}(w)$  ist ein Spezialfall der Funktion

$$G_{p,q}^{m,n} \left( w \left| \begin{array}{c} a_1, \dots, a_p \\ b_1, \dots, b_q \end{array} \right. \right),$$

die ich in meiner Arbeit [13] betrachtet habe. Es gilt nämlich <sup>8)</sup>

$$B_{p,r} \left( w \left| \begin{array}{c} a_1, \dots, a_p \\ b_1, \dots, b_{p+2} \end{array} \right. \right) = G_{p,p+2}^{r+2,p-r} \left( w \left| \begin{array}{c} a_1, \dots, a_p \\ b_1, \dots, b_{p+2} \end{array} \right. \right). \quad (16)$$

Also hat man <sup>9)</sup>

$$K_\nu(z) = \frac{1}{2} B_{0,0} \left( \frac{1}{4} z^2 \left| \frac{1}{2} \nu, -\frac{1}{2} \nu \right. \right), \quad (17)$$

$$W_{k,m}(z) = \frac{2^{k-\frac{1}{2}} z^{\frac{1}{2}} e^{\frac{1}{2}z}}{\sqrt{\pi}} B_{2,2} \left( \frac{1}{4} z^2 \left| \begin{array}{c} \frac{1}{4} - \frac{1}{2} k, \frac{3}{4} - \frac{1}{2} k \\ \frac{1}{2} m, \frac{1}{2} + \frac{1}{2} m, -\frac{1}{2} m, \frac{1}{2} - \frac{1}{2} m \end{array} \right. \right), \quad (18)$$

<sup>7)</sup> Die Ungleichungen (11) bis (15) sind stets lösbar; man setze zum Beispiel  $\beta = \frac{1}{2} \alpha$ .

<sup>8)</sup> Beziehung (16) ergibt sich sofort aus der Definition der Funktionen  $B_{p,r}(w)$  und  $G_{p,q}^{m,n}(w)$  (siehe Formel (5) der vorliegenden Abhandlung und Relation (6) von [13]).

<sup>9)</sup> Die Relationen (17), (18), (19), (20) und (23) folgen mit Hilfe von (16) aus (39), (22), (19), (30) und (47) von [13]. Der Beweis der Formeln (21) und (22) ist dem Beweis der Beziehungen (30) und (47) von [13] analog.

$$W_{k,m}(z) W_{-k,m}(z) = \frac{z}{2\sqrt{\pi}} B_{2,2} \left( \frac{1}{4} z^2 \left| \begin{matrix} \frac{1}{2} + k, \frac{1}{2} - k \\ 0, \frac{1}{2}, m, -m \end{matrix} \right. \right), \quad (19)$$

$$K_\nu(z) K_\mu(z) = \frac{1}{2\sqrt{\pi}} B_{2,2} \left( z^2 \left| \begin{matrix} 0, \frac{1}{2} \\ \frac{1}{2}\nu + \frac{1}{2}\mu, \frac{1}{2}\nu - \frac{1}{2}\mu, \frac{1}{2}\mu - \frac{1}{2}\nu, -\frac{1}{2}\nu - \frac{1}{2}\mu \end{matrix} \right. \right), \quad (20)$$

$$I_\nu(z) K_\mu(z) = \frac{1}{2\sqrt{\pi}} B_{2,0} \left( z^2 \left| \begin{matrix} 0, \frac{1}{2} \\ \frac{1}{2}\nu + \frac{1}{2}\mu, \frac{1}{2}\nu - \frac{1}{2}\mu, \frac{1}{2}\mu - \frac{1}{2}\nu, -\frac{1}{2}\nu - \frac{1}{2}\mu \end{matrix} \right. \right), \quad (21)$$

$$I_{-\nu}(z) - \mathbf{L}_\nu(z) = \frac{\cos \nu \pi}{\pi} B_{1,0} \left( \frac{1}{4} z^2 \left| \begin{matrix} \frac{1}{2} + \frac{1}{2}\nu \\ -\frac{1}{2}\nu, \frac{1}{2} + \frac{1}{2}\nu, \frac{1}{2}\nu \end{matrix} \right. \right), \quad (22)$$

$$I_\nu(z) - \mathbf{L}_\nu(z) = \frac{1}{\pi} B_{1,0} \left( \frac{1}{4} z^2 \left| \begin{matrix} \frac{1}{2} + \frac{1}{2}\nu \\ \frac{1}{2}\nu, \frac{1}{2} + \frac{1}{2}\nu, -\frac{1}{2}\nu \end{matrix} \right. \right). \quad (23)$$

Mit Hilfe des obigen Satzes kann man nun Integraldarstellungen für die in den linken Seiten der Relationen (17) bis (23) vorkommenden Funktionen ableiten. Die so erhaltenen Integralformeln (nämlich die Integralformeln (48), (55), (56), (57), (60), (65) und (66)) sind, soviel ich weisz, bisher noch nicht gegeben worden. Einige Spezialfälle waren aber schon bekannt.

## § 1. Vorbemerkungen über BESSELSche und LEGENDRESche Funktionen.

1. Für alle Werte von  $\nu$  und  $z$  gilt <sup>10)</sup>

$$J_\nu(z) = \left(\frac{1}{2}z\right)^\nu \sum_{m=0}^{\infty} \frac{(-1)^m z^{2m}}{2^{2m} m! \Gamma(\nu + m + 1)}. \quad (24)$$

2. Die Funktion  $J_\nu(z)$  besitzt für grosse Werte von  $|z|$  eine asymptotische Entwicklung der Gestalt

$$\begin{aligned} J_\nu(z) \sim \frac{1}{z^{\frac{1}{2}}} \left\{ \cos\left(z - \frac{1}{2}\nu\pi - \frac{1}{4}\pi\right) \left(A_0 + \frac{A_2}{z^2} + \dots\right) \right. \\ \left. + \sin\left(z - \frac{1}{2}\nu\pi - \frac{1}{4}\pi\right) \left(\frac{A_1}{z} + \frac{A_3}{z^3} + \dots\right) \right\}. \quad (25) \end{aligned}$$

3. Ist  $\Re(\beta - s) > 0$  und  $\Re(\beta - \alpha - 2s) < \frac{1}{2}$ , so gilt

$$\int_0^\infty u^{\beta - \alpha - 2s} J_{\alpha + \beta - 1}(2u) du = \frac{1}{2} \frac{\Gamma(\beta - s)}{\Gamma(\alpha + s)}. \quad (26)$$

<sup>10)</sup> Für (24), (25) und (26) vergl. man WATSON, [16], S. 40–43, 199 und 391. Die in (25) vorkommenden Zahlen  $A$  sind nicht von  $z$  abhängig.

Die folgenden Beziehungen (27) bis (31) (inkl.) kommen bei HOBSON und Herrn BARNES vor<sup>11)</sup>:

4. Ist  $\left| \frac{v-1}{v+1} \right| < 1$ , so gilt

$$P_n^m(v) = \frac{1}{\Gamma(1-m)} \left( \frac{v+1}{v-1} \right)^{\frac{1}{2}m} \left( \frac{1}{2} + \frac{1}{2}v \right)^n {}_2F_1 \left( -n, -n-m; 1-m; \frac{v-1}{v+1} \right). \quad (27)$$

5. Ist  $|\arg w| < \frac{1}{2}\pi$  und  $m \neq 1, 2, 3, \dots$ , so gilt

$${}_2F_1 \left( \frac{1}{2} - \frac{1}{2}m + \frac{1}{2}n, -\frac{1}{2}m - \frac{1}{2}n; 1-m; -w^2 \right) = 2^{-m} \Gamma(1-m) w^m P_n^m(\sqrt{1+w^2}). \quad (28)$$

6. Ist  $|\arg v| < \pi$  und  $|\arg(v \pm 1)| < \pi$ , so gilt

$$\frac{1}{\Gamma(1+n+m)} Q_n^m(v) = \frac{e^{m\pi i} \sqrt{\pi} (v^2-1)^{\frac{1}{2}m}}{2^{n+1} v^{n+m+1} \Gamma(\frac{3}{2}+n)} \left\{ \begin{array}{l} \times {}_2F_1 \left( 1 + \frac{1}{2}n + \frac{1}{2}m, \frac{1}{2} + \frac{1}{2}n + \frac{1}{2}m; \frac{3}{2} + n; \frac{1}{v^2} \right) \end{array} \right\} \quad (29)$$

7. Ist  $|\arg v| < \frac{1}{2}\pi$  und  $n+m \neq -1, -2, -3, \dots$ , so gilt

$$Q_n^m(\pm i v) = e^{(m \mp \frac{1}{2}n \mp \frac{1}{2})\pi i} 2^{m-1} \sqrt{\pi} (1+v^2)^{\frac{1}{2}m} \times \left\{ \begin{array}{l} - \frac{2 \Gamma(1 + \frac{1}{2}n + \frac{1}{2}m) v}{\Gamma(\frac{1}{2} + \frac{1}{2}n - \frac{1}{2}m)} {}_2F_1 \left( 1 + \frac{1}{2}n + \frac{1}{2}m, \frac{1}{2} - \frac{1}{2}n + \frac{1}{2}m; \frac{3}{2}; -v^2 \right) \\ + \frac{\Gamma(\frac{1}{2} + \frac{1}{2}n + \frac{1}{2}m)}{\Gamma(1 + \frac{1}{2}n - \frac{1}{2}m)} {}_2F_1 \left( \frac{1}{2} + \frac{1}{2}n + \frac{1}{2}m, -\frac{1}{2}n + \frac{1}{2}m; \frac{1}{2}; -v^2 \right) \end{array} \right\}. \quad (30)$$

8. Ist  $m$  nicht ganz, so gilt

$$\frac{2 e^{-m\pi i}}{\Gamma(1+n+m)} Q_n^m(v) = \frac{\pi}{\sin m\pi} \left\{ \frac{1}{\Gamma(1+n+m)} P_n^m(v) - \frac{1}{\Gamma(1+n-m)} P_n^{-m}(v) \right\}. \quad (31)$$

Nun hat man<sup>12)</sup>

$$\begin{aligned} & {}_3F_2(2a, 2b, a+b; a+b+\tfrac{1}{2}, 2a+2b-1; v) \\ &= {}_2F_1(a, b; a+b+\tfrac{1}{2}; v) \cdot {}_2F_1(a-\tfrac{1}{2}, b-\tfrac{1}{2}; a+b-\tfrac{1}{2}; v) (1-v)^{-\frac{1}{2}} \end{aligned}$$

und

$$\begin{aligned} & {}_3F_2(2a+1, 2b, a+b; a+b+\tfrac{1}{2}, 2a+2b; v) \\ &= {}_2F_1(a, b; a+b+\tfrac{1}{2}; v) \cdot {}_2F_1(a+\tfrac{1}{2}, b-\tfrac{1}{2}; a+b+\tfrac{1}{2}; v) (1-v)^{-\frac{1}{2}}. \end{aligned}$$

<sup>11)</sup> Man vergl.: HOBSON, [9], S. 456, 462 und 467—468; [10], S. 195, 204, 210, 215—216 und 219. BARNES, [5], S. 103, 120, 122 und 124. Siehe auch Fußnote 2).

<sup>12)</sup> Siehe ORR, [15], S. 13, Formel (59) und S. 12, Formel (5c). Man vergl. auch BAILEY, [1], S. 381 und GOURSAT, [8], S. 416.



Ich finde daher mit Rücksicht auf (28)

9. Ist  $|\arg w| < \frac{1}{2}\pi$  und  $\lambda \neq \frac{1}{2}, \frac{3}{2}, \frac{5}{2}, \dots$ , so gilt

$$\left. \begin{aligned} & {}_3F_2(1-\lambda+\nu, 1-\lambda-\nu, 1-\lambda; \frac{3}{2}-\lambda, 1-2\lambda; -w^2) \\ & = {}_2F_1(\frac{1}{2}-\frac{1}{2}\lambda+\frac{1}{2}\nu, \frac{1}{2}-\frac{1}{2}\lambda-\frac{1}{2}\nu; \frac{3}{2}-\lambda; -w^2) \\ & \times {}_2F_1(-\frac{1}{2}\lambda+\frac{1}{2}\nu, -\frac{1}{2}\lambda-\frac{1}{2}\nu; \frac{1}{2}-\lambda; -w^2) (1+w^2)^{-\frac{1}{2}} \\ & = 2^{-2\lambda} \Gamma(\frac{3}{2}-\lambda) \Gamma(\frac{1}{2}-\lambda) w^{2\lambda} P_{\nu-\frac{1}{2}}^{\lambda-\frac{1}{2}}(\sqrt{1+w^2}) P_{\nu+\frac{1}{2}}^{\lambda+\frac{1}{2}}(\sqrt{1+w^2}) (1+w^2)^{-\frac{1}{2}}. \end{aligned} \right\} \quad (32)$$

10. Ist  $|\arg w| < \frac{1}{2}\pi$  und  $\lambda \neq 1, 2, 3, \dots$ , so gilt

$$\left. \begin{aligned} & {}_3F_2(\frac{3}{2}-\lambda+\nu, \frac{1}{2}-\lambda-\nu, \frac{1}{2}-\lambda; 1-\lambda, 1-2\lambda; -w^2) \\ & = {}_2F_1(\frac{1}{4}-\frac{1}{2}\lambda+\frac{1}{2}\nu, \frac{1}{4}-\frac{1}{2}\lambda-\frac{1}{2}\nu; 1-\lambda; -w^2) \\ & \times {}_2F_1(\frac{3}{4}-\frac{1}{2}\lambda+\frac{1}{2}\nu, -\frac{1}{4}-\frac{1}{2}\lambda-\frac{1}{2}\nu; 1-\lambda; -w^2) (1+w^2)^{-\frac{1}{2}} \\ & = 2^{-2\lambda} \Gamma^2(1-\lambda) w^{2\lambda} P_{\nu-\frac{1}{2}}^{\lambda}(\sqrt{1+w^2}) P_{\nu+\frac{1}{2}}^{\lambda}(\sqrt{1+w^2}) (1+w^2)^{-\frac{1}{2}}. \end{aligned} \right\} \quad (33)$$

In einer vorigen Arbeit<sup>13)</sup> habe ich schon bewiesen:

11. Ist  $|\arg w| < \frac{1}{2}\pi$  und  $\lambda \neq 1, 2, 3, \dots$ , so gilt

$$\left. \begin{aligned} & {}_3F_2(\frac{1}{2}-\lambda+\nu, \frac{1}{2}-\lambda-\nu, \frac{1}{2}-\lambda; 1-\lambda, 1-2\lambda; -w^2) \\ & = 2^{-2\lambda} \Gamma^2(1-\lambda) w^{2\lambda} \{P_{\nu-\frac{1}{2}}^{\lambda}(\sqrt{1+w^2})\}^2. \end{aligned} \right\} \quad (34)$$

12. Ist  $|\arg w| < \frac{1}{2}\pi$  und  $\lambda \neq \pm 1, \pm 2, \pm 3, \dots$ , so gilt

$$\left. \begin{aligned} & {}_3F_2(\frac{1}{2}+\nu, \frac{1}{2}-\nu, \frac{1}{2}; 1+\lambda, 1-\lambda; -w^2) \\ & = \Gamma(1+\lambda) \Gamma(1-\lambda) P_{\nu-\frac{1}{2}}^{\lambda}(\sqrt{1+w^2}) P_{\nu-\frac{1}{2}}^{-\lambda}(\sqrt{1+w^2}). \end{aligned} \right\} \quad (35)$$

Aus (34) und (35) ergibt sich noch:

13. Ist  $\lambda$  nicht ganz und  $\frac{1}{2}-\lambda+\nu \neq 0, -1, -2, \dots$ , so gilt

$$\left. \begin{aligned} & \frac{\Gamma(\frac{1}{2}-\lambda+\nu) \Gamma(\lambda)}{\Gamma(\frac{1}{2}+\lambda+\nu) \Gamma(-\lambda)} \left(\frac{2}{w}\right)^{2\lambda} {}_3F_2(\frac{1}{2}-\lambda+\nu, \frac{1}{2}-\lambda-\nu, \frac{1}{2}-\lambda; 1-\lambda, 1-2\lambda; -w^2) \\ & + {}_3F_2(\frac{1}{2}+\nu, \frac{1}{2}-\nu, \frac{1}{2}; 1+\lambda, 1-\lambda; -w^2) \\ & = -\frac{\lambda\pi}{\sin\lambda\pi} \left[ \frac{\Gamma(\frac{1}{2}-\lambda+\nu)}{\Gamma(\frac{1}{2}+\lambda+\nu)} \{P_{\nu-\frac{1}{2}}^{\lambda}(\sqrt{1+w^2})\}^2 - P_{\nu-\frac{1}{2}}^{\lambda}(\sqrt{1+w^2}) P_{\nu-\frac{1}{2}}^{-\lambda}(\sqrt{1+w^2}) \right] \\ & = -\frac{2\lambda e^{-\lambda\pi i} \Gamma(\frac{1}{2}-\lambda+\nu)}{\Gamma(\frac{1}{2}+\lambda+\nu)} P_{\nu-\frac{1}{2}}^{\lambda}(\sqrt{1+w^2}) Q_{\nu-\frac{1}{2}}^{\lambda}(\sqrt{1+w^2}) \end{aligned} \right\} \quad (36)$$

(wegen (31) mit  $n = \nu - \frac{1}{2}$ ,  $m = \lambda$  und  $v = \sqrt{1+w^2}$  angewendet).

<sup>13)</sup> MEIJER, [14], § 6; der in [14] gegebene Beweis der Beziehungen (34) und (35) ist dem Beweis von (32) und (33) analog.

§ 2. Beweis des Satzes <sup>14)</sup>.

Nach (6) hat man

$$0 \leq p, \quad 1 \leq p-r+1 \leq p+1. \quad \dots \quad (37)$$

Wegen (11) und (12) gilt  $\Re(a+b_j) > -\frac{1}{4}$  ( $j=1, \dots, r+2$ ), so dass aus (15) folgt

$$1-a-b_j \neq 1, 2, 3, \dots \quad (j=1, \dots, r+2). \quad \dots \quad (38)$$

Aus (37), (7), (14), (8) und (38) ergibt sich, dass die in der rechten Seite von (10) vorkommende Funktion  $\Psi_{p, p-r+1}$  einen Sinn hat (siehe (2), (3) und (4)).

Ist  $\zeta \neq 0$  und  $|\arg \zeta| < \pi$ , so besitzt die durch (1) definierte Funktion  $\Psi_{p,q}(\zeta)$  die folgende Integraldarstellung:

$$\Psi_{p,q} \left( \zeta \begin{matrix} c_1, \dots, c_{p+2} \\ b_1, \dots, b_{p+2} \end{matrix} \right) = \left. \begin{aligned} &= \frac{1}{2\pi i} \int_L \frac{\prod_{h=1}^q \Gamma(1-c_h+s) \prod_{h=1}^{p-q+3} \Gamma(b_h-s)}{\prod_{h=q+1}^{p+2} \Gamma(c_h-s) \prod_{h=p-q+4}^{p+2} \Gamma(1-b_h+s)} \zeta^{-s} ds; \end{aligned} \right\} \quad (39)$$

hierin läuft der Integrationsweg  $L$  von  $-\infty i + \tau$  nach  $\infty i + \tau$  ( $\tau$  ist eine beliebige reelle Zahl) und zwar so, dass die Punkte  $c_h-1, c_h-2, c_h-3, \dots$  ( $h=1, \dots, q$ ) auf der linken, die Punkte  $b_h, b_h+1, b_h+2, \dots$  ( $h=1, \dots, p-q+3$ ) aber auf der rechten Seite von  $L$  liegen <sup>15)</sup>. Denn die linke Seite von (39) ist gleich der Summe der Residuen des letzten Integranden in den Polen auf der linken Seite von  $L$  <sup>16)</sup>.

Aus (39) folgt auch <sup>17)</sup>

$$\Psi_{p,q} \left( \zeta \begin{matrix} c_1, \dots, c_{p+2} \\ b_1, \dots, b_{p+2} \end{matrix} \right) = \left. \begin{aligned} &= \sum_{j=1}^{p-q+3} \frac{\prod_{h=1}^q \Gamma(1+b_j-c_h) \prod_{\substack{h=1 \\ h \neq j}}^{p-q+3} \Gamma(b_h-b_j)}{\prod_{h=q+1}^{p+2} \Gamma(c_h-b_j) \prod_{h=p-q+4}^{p+2} \Gamma(1+b_j-b_h)} \zeta^{-b_j} \times \\ &\times {}_{p+2}F_{p+1} \left( 1+b_j-c_1, \dots, 1+b_j-c_{p+2}; 1+b_j-b_1, \dots, 1+b_j-b_{p+2}; -\frac{1}{\zeta} \right). \end{aligned} \right\} \quad (40)$$

<sup>14)</sup> Dieser Beweis hat eine grosse Ähnlichkeit mit dem von Satz 4 meiner Arbeit [13].

<sup>15)</sup> Dies ist möglich wegen (4).

<sup>16)</sup> Man vergl. BARNES, [4], S. 146. Herr BARNES betrachtet nur die gewöhnliche hypergeometrische Funktion  ${}_2F_1$ . Siehe auch WHITTAKER and WATSON, [17], S. 286–289.

<sup>17)</sup> Ich berechne jetzt die Summe der Residuen des Integranden in den Polen auf der rechten Seite von  $L$ . Formel (40) gilt, wofern nicht nur (3) und (4) erfüllt sind, sondern auch noch  $b_h - b_j$  nicht ganz ist ( $h=1, \dots, p-q+3$ ;  $j=1, \dots, p-q+3$ ;  $h \neq j$ ).



Aus (46) und (26) geht jetzt hervor <sup>19)</sup>

$$\begin{aligned}
 & 2\pi i \int_0^\infty u^{\beta-\alpha} J_{\alpha+\beta-1}(2u) \Psi_{p,p-r+1} \left( \frac{u^2}{w} \left| \begin{matrix} 1-\alpha, a_1, \dots, a_p, \beta \\ b_1, \dots, b_{p+2} \end{matrix} \right. \right) du \\
 &= \int_0^\infty u^{\beta-\alpha} J_{\alpha+\beta-1}(2u) du \int_{.1} \frac{\Gamma(\alpha+s) \prod_{j=1}^{p-r} \Gamma(1-a_j+s) \prod_{j=1}^{r+2} \Gamma(b_j-s)}{\Gamma(\beta-s) \prod_{j=p-r+1}^p \Gamma(a_j-s) \prod_{j=r+3}^{p+2} \Gamma(1-b_j+s)} \left( \frac{u^2}{w} \right)^{-s} ds \\
 &= \int_{.1} \frac{\Gamma(\alpha+s) \prod_{j=1}^{p-r} \Gamma(1-a_j+s) \prod_{j=1}^{r+2} \Gamma(b_j-s)}{\Gamma(\beta-s) \prod_{j=p-r+1}^p \Gamma(a_j-s) \prod_{j=r+3}^{p+2} \Gamma(1-b_j+s)} w^s ds \int_0^\infty u^{\beta-\alpha-2s} J_{\alpha+\beta-1}(2u) du \\
 &= \frac{1}{2} \int_{.1} \frac{\prod_{j=1}^{p-r} \Gamma(1-a_j+s) \prod_{j=1}^{r+2} \Gamma(b_j-s)}{\prod_{j=p-r+1}^p \Gamma(a_j-s) \prod_{j=r+3}^{p+2} \Gamma(1-b_j+s)} w^s ds.
 \end{aligned}$$

Die rechte Seite dieser Relation ist aber gleich <sup>20)</sup>

$$\pi i B_{p,r} \left( w \left| \begin{matrix} a_1, \dots, a_p \\ b_1, \dots, b_{p+2} \end{matrix} \right. \right).$$

Hiermit ist der Satz bewiesen.

<sup>19)</sup> Die Vertauschung der Integrationsfolge ist erlaubt wegen (47); man vergl. BROMWICH, [6], § 177.

<sup>20)</sup> Ich berechne die Summe der Residuen des Integranden in den Polen auf der rechten Seite von A. Man vergl. BARNES, [2], S. 295–296; [3], S. 65–71.

**Plantkunde.** — *Verschillen in het bloemvormende vermogen van Narcis en Hyacinth.* Door J. D. GERRITSEN en W. G. v. D. KLOOT. (Mededeeling N<sup>o</sup>. 47 van het Laboratorium voor Plantenphysiologisch Onderzoek te Wageningen.) (Aangeboden door Prof. A. H. BLAAUW.)

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*Narcissus Pseudonarcissus* vormt de bloem in Mei en Juni tijdens de assimilatieperiode, vóórdat de bollen gerooid worden (HUISMAN en HARTSEMA, 1933). Hyacinthen leggen de bloeiwijze aan na het rooien. Deze laatste bollen waren daardoor evenals tulpen zoo geschikt voor het vaststellen van den invloed van de temperatuur op de bloemvorming. Het tempo der bloemvorming werd destijds in stippencurven uitgedrukt voor verschillende temperaturen (BLAAUW, 1924 en LUYTEN, JOUSTRA en BLAAUW, 1925).

De tulp laat een optimum zien bij ongeveer 20° C., de hyacinth bij  $\pm 25\frac{1}{2}^{\circ}$  C. Voor een vergelijking was het van belang te weten, hoe in dit opzicht de narcis zich zou gedragen, ook al zou hier de practische toepassing, tenzij door bodemverwarming, van weinig of geen beteekenis zijn in tegenstelling met hyacinthen en tulpen.

Hiertoe werd een partij bollen van gemidd. 15—17 cm omtrek gerooid op 2 Mei en na het verwijderen van bladeren en wortels werden bij 9°, 13°, 17°, 20°, 23°,  $25\frac{1}{2}^{\circ}$  en 28° C. elk 60 bollen geplaatst, waarvan er na 2, 4, 6, 8, 10 en 12 weken 10 werden gefixeerd uit elke temperatuur. Deze proef ging uit van de ervaring bij hyacinthen opgedaan, (BLAAUW, 1920), dat bollen van dergelijke zwaarte op elken tijd van het jaar — bijv. in Januari — gerooid en bij  $25\frac{1}{2}^{\circ}$  C. gelegd, aan hun groeipunt ophouden met bladvorming en overgaan tot vorming van een nieuwe bloemtros (naast de reeds bestaande). De datum 2 Mei was gekozen, omdat in twee vorige jaren het begin van de bloemvorming dan nog juist niet begonnen was. Ter contrôle werden op 2 Mei 10 bollen gefixeerd.

Bij onderzoek van deze contrôle-bollen bleek nu, dat op 2 Mei 4 stuks nog volkomen in stadium I verkeerden, verder één in St. I à II en één in II (= vergroot groeipunt), terwijl bij 4 reeds de afsplitsing van de spatha begon (= stad. II+). De proef was dus iets te laat begonnen, naar onze opvatting.

Maar wat bleek achteraf tot einde Juli in de bollen te gebeuren? Wanneer wij eerst den uitslag van de 4 fixaties in Juni en Juli samenvoegen, omdat pas in Juni met zekerheid het al of niet bloemvormen, vooral bij 9° C. en 13° C. is vast te stellen, dan blijken van deze 280 bollen uit 7 temperaturen slechts 111 bloemen gevormd te hebben, dat is 40 %. Niet-gerooidde bollen van deze partij hadden alle normaal bloem aan-



gelegd; bij 't afpellen bleken de 420 behandelde bollen ook in het voorjaar alle gebloeid te hebben.

Het aantal geslaagde bloemen van 40 % stemt merkwaardig overeen met 't aantal dat op 2 Mei reeds even met bloemvorming is begonnen.

Het blijkt uit een en ander: 1<sup>o</sup>. *dat wanneer de bloemvorming nog niet is begonnen* (stadium I) *de bloemvorming in deze gerooide bollen niet op gang kan komen* ondanks den overvloed aan reservestoffen, in tegenstelling dus met de hyacinth; — en 2<sup>o</sup>. *dat wanneer de bloemvorming slechts even is ingeleid* (begin spathavorming), *de bloem volkomen normaal kan gereed komen*. Vooral ook dit laatste punt is opvallend. Men zou daaruit kunnen afleiden, dat wanneer wij uitwendig stadium II<sup>+</sup> waarnemen, de bestemming van de cellen of celgroepen voor alle bloemdeelen reeds is vastgelegd, reeds is gedifferentieerd in de dieper gelegen lagen. Heel waarschijnlijk is dit echter niet, daar er nog wel 6 tot 8 weken verlopen, voordat de meeldraden en vruchtbladen als primordia zichtbaar worden (stadium VI, VII en VIII). Toch moet er in ieder geval een zekere phase gepasseerd zijn, om de geheele verdere bloemvorming mogelijk te maken.

Intusschen scheen de grens van het al of niet kunnen slagen wel eenigszins afhankelijk van de temperatuur te zijn.

Op 40 bollen gelukten:

bij 9° C. 22 bloemen		bij 23° C. 11 bloemen
„ 13° C. 26 „		„ 25½° C. 11 „
„ 17° C. 17 „		„ 28° C. 8 „
„ 20° C. 16 „		

Hieruit zou men afleiden, dat 9° C. en 13° C. 't gunstigst werken; uit latere proeven (zie slot) bleek weer dat 13° C. volstrekt niet gunstiger zou zijn dan 20° C., zoodat dit groot aantal geslaagde bloemen bij 13° en 9° C. ook wel op toeval zou kunnen berusten, wanneer er in die groepen meer bollen boven stadium II waren terecht gekomen. Wel schijnt ons de minder gunstige werking van hooge temperaturen (23°—28° C.) vrij zeker, zoodat de bloemvorming waarschijnlijk lichter blijft hokken in een stadium, waarin bij 20° C. en lager de bloem vlot voltooid wordt.

Hier volgt reeds uit, dat dit wèl of nièt bloem kunnen vormen geen absoluut scherpe grens is; en zoo is het ook begrijpelijk, dat er af en toe gevallen werden aangetroffen — in deze eerste proef tot  $\pm 10\%$  — waarbij overgangsvormen ontstonden: terwijl na meestal 3 gewone loofblaadjes de spatha behoort te volgen, werd in deze gevallen een wat vervormd blaadje aangetroffen, soms meer loofbladachtig, soms vrij sterk spatha-achtig. Na dit afwijkende blad, had het groeppunt dan weer geheel normale blaadjes afgesplitst. Blijkbaar had in deze gevallen het groeppunt op 2 Mei juist op de grens der bloemvorming gestaan.

In de vele gevallen, waarin dus geen bloem werd gevormd, bleek het groeppunt ondanks het rooien der bollen, wel in staat om voort te gaan met het afsplitsen van blaadjes.

TABEL 1.  
Gemidd. aantal afgesplitste blaadjes (na de 3 of 4 scheedebladen) bij  
niet-bloemvormende bollen ( $n = 10$ ).

Op 2 Mei 3.1	2 w. 16 Mei	4 w. 30 Mei	6 w. 13 Juni	8 w. 27 Juni	10 w. 11 Juli	12 w. 25 Juli
9°	3.0	3.2	3.5	3.8	3.6	4.2
13°	3.0	3.3	3.8	4.0	4.1	4.5
17°	3.0	3.6	4.0	4.3	4.8	5.1
20°	3.4	4.0	4.3	4.3	4.4	4.7
23°	3.5	3.9	4.3	4.4	4.4	4.9
25½°	3.3	3.8	4.0	4.1	4.2	4.0
28°	3.3	3.7	3.9	3.8	3.9	3.9

In de gunstige temperaturen worden — in de plaats van bloemvorming — nog 2 (soms wel eens 3) blaadjes na 2 Mei afgesplitst. Het gemiddelde vertoont eerst een optimum voor dezen bladaanleg, dat boven 20° C. ligt, maar dat bij langen duur naar lager (17°) verschuift. Ook hier bij orgaan-aanleg zien wij dus daling van het optimum door den duur, zooals dat in vroegere mededeelingen, vooral voor den groei, reeds meermalen is vermeld.

Dit typeerend verschijnsel van een *verschuivend optimum* viel ook te constateeren door het meten der lengte van het 1<sup>e</sup> loofblaadje van den knop, dat dus reeds lang te voren was aangelegd, maar dat pas het volgend jaar voor de assimilatie uitgroeit. Fig. 1 vertoont ook duidelijk

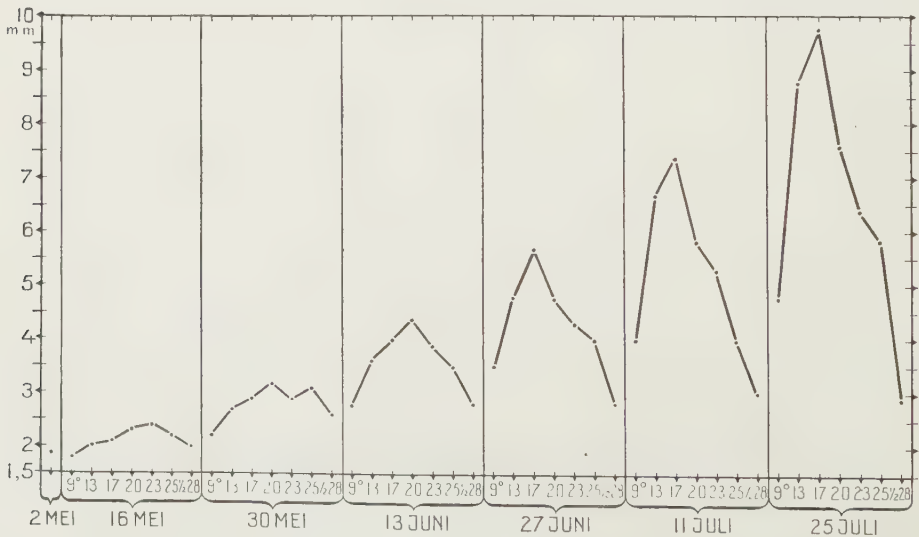


Fig. 1. Gemiddelde lengte van het eerste loofblad van den knop in mm., van 2 Mei af in verschillende temperaturen.

(Average-length of the first leaflet of the bud in different temperatures.)

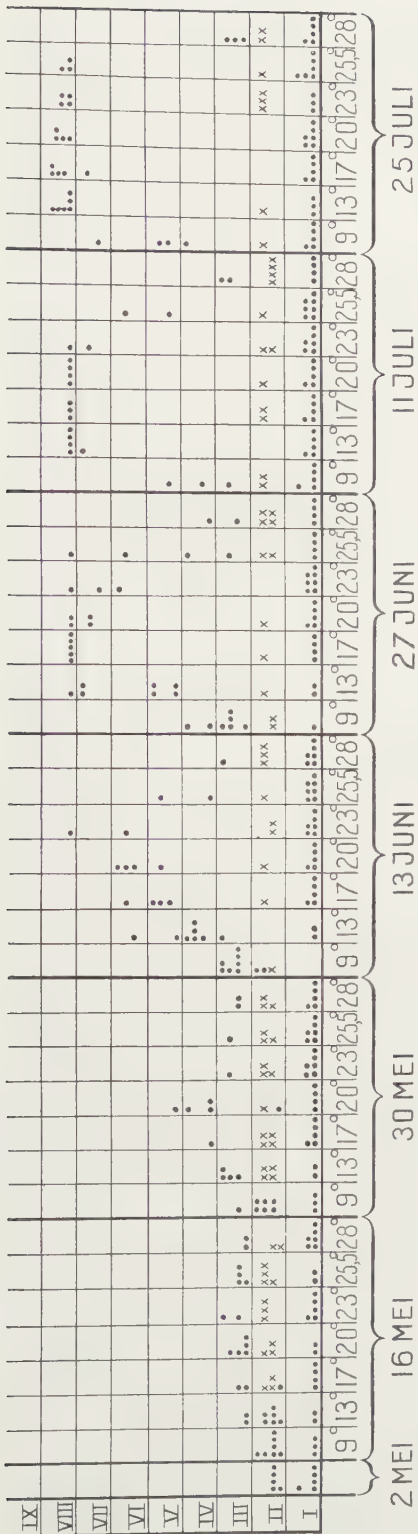


Fig. 2. Bloemvorming en temperatuur van de Narcis; elke stip geeft het stadium (I—IX) van elken bol. × × bollen met een half-spathavormig 4e loofblad, welke meestal bladvormend blijven.

(Each dot indicates the stage of the flower-formation (I—IX) in the different temperatures. × × bulbs with a nearly spathe-like 4th leaflet, without succeeding to form a flower.)

dat bij blaadjes in dezen jongen toestand het optimum van  $23^{\circ}$  C. naar  $20^{\circ}$  C. en dan tot  $17^{\circ}$  C. daalt, terwijl na  $2\frac{1}{2}$  maand  $13^{\circ}$  C. zelfs gunstiger is dan  $20^{\circ}$  C.

Keeren wij nu tot ons oorspronkelijke doel terug: den invloed van de temperatuur op de bloemvormende periode, dan kunnen wij — ondanks het feit dat gemiddeld slechts 40 % van de bollen een normale bloemvorming kan doorloopen, toch daaraan nog voldoende zien. In zooverre was het dus een gelukkig toeval, dat de bollen op 2 Mei niet alle in stadium I verkeerden, zooals wij bedoelden, maar dat  $\pm 40$  % juist met den spatha-aanleg begon.

Volgens de gewoonte, die ook reeds bij hyacinth en tulp werd toegepast, werd de toestand op de verschillende data in stadia uitgedrukt en het stadium van elken bol door een stip in een z.g. stippencurve afgezet (Fig. 2).

Daarbij is de toestand van alle bollen opgegeven, zodat men ook de later in stadium I blijvende bollen weervindt. Met × zijn die bollen weergegeven waar het 4<sup>e</sup> loofblad abnormaal, half-spatha-achtig was. Men bedenke dat op 2 Mei in elk der 42 tientallen natuurlijk in zeer verschillende verhoudingen de stad. I tot II<sup>+</sup> terecht kwamen. Dit valt

vooral op bij 9° C. waar in Juni slechts 1 van de 20 bollen in stad. I bleef staan, maar in Juli 10 van de 20.

Letten wij nu verder op de boven stad. II stijgende exemplaren, die dus alle kunnen gelukken, dan zien we, ondanks het geringe aantal, bij samenvatting van 16 Mei, 30 Mei en 13 Juni, dat bij  $\pm 20^{\circ}$  C. het optimum in de snelheid der bloemvorming ligt; op den duur (27 Juni) wellicht iets meer bij 17° C.

Dit stemt dus overeen met het optimum van de tulp.

*Proef met hyacinthen.*

Na de ervaring, opgedaan bij de narcis, vraagt men zich nog eens af, of wel inderdaad de hyacinthenbol van ongeveer gelijk gewicht, onder zulke ingrijpende omstandigheden (in den winter gerooid en met afgesneden loof en wortels), in gunstige temperatuur een bloemtros kan maken.

Bollen van l'Innocence van 15—17 cm omtrek werden 20 Januari op 3 wijzen behandeld.

A. 12 bollen werden voorzichtig uitgegraven om de wortels zoo min mogelijk te beschadigen, in potten geplant en in  $25\frac{1}{2}^{\circ}$  C. geplaatst.

B. Van de 2<sup>e</sup> groep van 12 bollen werden alleen de wortels afgesneden; en na eenig drogen werden deze bollen in een thermostaat van  $25\frac{1}{2}^{\circ}$  C. met 75—80 % vochtigheid gelegd.

C. Van 12 bollen werden de wortels en uitkomende bladen (de „neus”) afgesneden; 2 dagen eenigszins gedroogd en daarna ook in de thermostaat van  $25\frac{1}{2}^{\circ}$  C. gelegd.

De geplante bollen (A) groeiden snel en kwamen reeds begin Februari in vollen bloei, dus in volkomen duister.

Van groep B groeide het loof nog eenigszins, maar trossen kwamen niet te voorschijn; terwijl groep C uiterlijk niets vertoonde, alleen soms iets inrotte bij de afgesneden neus.

Na ruim 8 weken (19 Mrt) werden alle bollen gefixeerd in alcohol en later onderzocht.

Het was dus nu de vraag wat de jonge knop (naast de bloemtros voor dit voorjaar, die in A in bloei raakte) zou doen. Deze knop bestaat in Januari uit een groeppunt, dat een paar scheedebleden (2—3) en enkele loofblaadjes gevormd heeft. Dit aantal loofblaadjes bedraagt in Jan. bij bollen van deze zwaarte meestal 3 à 4; het groeppunt verkeert midden in de bladvormende periode. In normale gevallen, zou buiten bij de daar heerscheende temperatuur dit bladaantal van meestal 5 à 6 in Januari nog tot 9 à 12 in 't einde van Juni stijgen (scheedebleden meegeteld).

De gevolgen van de temperatuur van  $25\frac{1}{2}^{\circ}$  C. zijn uit de onderstaande gegevens zichtbaar.

*Groep A.* 20 Jan.—19 Mrt in  $25\frac{1}{2}^{\circ}$  C.

Aantal blaadjes: 6—5—6—5—6— $5\frac{1}{2}$ —6—5—5—6—5—5.

Lengte gevormd trosje gemidd.: 5.9 mm. Stadium: 11 keer IX; VIII à IX. Aantal bloemen: 7 tot 12, gemidd. 9.2.

Doordat het groeipunt tot bloemvorming is overgegaan is er weer een nieuw vervangend groeipunt ontstaan, dat meestal reeds 3 soms 2 afsplitsingen (1 keer slechts 1) heeft gevormd. Door de optimale temperatuur van  $25\frac{1}{2}^{\circ}\text{C}$ . is zelfs in 5 van 12 bollen ook dit NVP alweer met een 2<sup>e</sup> bloemvorming begonnen (stadium I à II; II; II; III; V à VI).

*Groep B.* 22 Jan.—19 Mrt in  $25\frac{1}{2}^{\circ}\text{C}$ .

Aantal blaadjes: 5—5—9(!)—5—5—5—5—5—5—5—5.

Lengte gevormd trosje gemidd.: 4.6 mm. Stadium: 6 keer IX; IX—; IX—; VIII; VIII—; VII à VIII; I(!). Aantal bloemen 7 tot 10, gemidd. 8.5.

Het exemplaar met 9 blaadjes is degeen, die geen tros heeft gevormd (I). Het nieuwe groeipunt heeft in groep B 2 tot 3 afsplitsingen; maar is slechts 2 maal tot bloemvorming (VI- en II) overgegaan.

*Groep C.* 22 Jan.—19 Mrt in  $25\frac{1}{2}^{\circ}\text{C}$ .

Aantal blaadjes: 5—5—5—4—6—6—5—7—6—5—5—5.

Lengte gevormd trosje gemidd.: 4.4 mm. Stadium: 10 keer IX; IX—; VIII à IX. Aantal bloemen 5 tot 10, gemidd. 7.2.

Het nieuwe groeipunt heeft ook hier 2 tot 3 afsplitsingen, maar is in geen geval tot herhaalde bloemvorming overgegaan.

*Conclusie:* In alle 3 groepen wordt de bladvormende periode (meest 5 à 6 blaadjes) afgebroken en treedt (bij  $25\frac{1}{2}^{\circ}\text{C}$ .) bloemvorming in, zoodat na 8 weken een volkomen bloemtros is aangelegd. Bij slechts 1 van de 36 bollen is het groeipunt bladvormend gebleven. In tegenstelling met de narcis heeft de hyacinth voor deze bloemvorming de assimilatie (of de bodemwater-opname) van dit jaar niet nodig; zij heeft aan de aanwezige reservestoffen voldoende. Intusschen mag niet vergeten worden, dat onder deze abnormale omstandigheden wel het aantal bloemen per tros geringer blijft, dan wanneer de bloemaanleg op normale wijze een half jaar later had plaats gevonden.

Tusschen de groepen valt een klein verschil op te merken dat waarschijnlijk wel reëel is bij een gemiddelde uit 12 bollen: het gevormde trosje is iets langer en het aantal gevormde bloemen iets grooter wanneer de bollen, hoewel in 't donker, weer geplant worden zonder dat bladen of wortels worden afgesneden. Ook blijkt dit iets sterker bloeivermogen uit het tamelijk vaak inleiden van een 2<sup>e</sup> trosje.

#### *Herhaling van de proef met de narcis.*

In een ander jaar werd de vraag omtrent het al of niet vormen van bloemen bij de narcis herhaald.

Op 23 April, als er nog geen begin van bloemvorming is, en op 20 Mei, als dit wel het geval pleegt te zijn, werden telkens 40 stuks gerooid, wortels en loof afgesneden en daarna 20 bij  $13^{\circ}\text{C}$ . en 20 bij  $20^{\circ}\text{C}$ . gelegd.

In de eerst vermelde proef toch scheen bij  $13^{\circ}\text{C}$ . de kans op gelukken



vrij wat gunstiger dan bij 20° C.; anderzijds bewees de temperatuurproef, dat 20° C. wel gunstig was voor het vlug optreden van den bloemaanleg.

Bovendien werd op 23 April, 20 Mei en 5 Juni ook van telkens 20 stuks, die buiten bleven staan, alléén het loof afgesneden, terwijl 10 stuks op die data voor contrôle werden gefixeerd.

Op 31 Juli werden alle 20-tallen uit 13° C., 20° C. en uit de 3 groepen van buiten gefixeerd voor onderzoek, en bovendien een 20-tal Narcissen van dezelfde groep, niet afgesneden, ter contrôle.

I. De contrôle op 23 April toonde dat alle 10 bollen nog in stadium I verkeerden; het 3<sup>e</sup> loofblad werd juist zichtbaar.

De toen gerooide bollen bleken op 31 Juli noch bij 13° C., noch bij 20° C. bloem te hebben gevormd; in plaats daarvan had het groeipunt 1 of 2 blaadjes bijgevormd.

II. De contrôle op 20 Mei was iets minder ver dan wij op grond van vorige jaren mochten verwachten. Zij vertoonde 2 maal stadium II<sup>+</sup>, 4 maal stadium II, verder stad. II<sup>-</sup>, I à II, I à II en I<sup>+</sup>.

Van de op 20 Mei gerooide bollen hadden op 31 Juli bij 13° C. slechts 14 en bij 20° C. maar 15 een bloem gevormd (alle in stadium VIII of iets verder); er waren dus resp. 6 en 5 in stadium I gebleven. Dit nu stemt overeen met hetgeen de fixatie van 20 Mei kon doen verwachten. De bloemvorming was toen nog niet ver genoeg ingeleid.

Een en ander (I en II) is in overeenstemming met het vroeger gevondene, dat *wanneer stadium II nog niet is bereikt, er geen bloemaanleg onder die omstandigheden plaats heeft; maar dat in stad. II of iets verder de bol in staat is de volledige bloemvorming tot stand te brengen.*

Echter wordt hier niet bevestigd, dat bij 13° C. meer bloemen nog zouden gelukken dan bij 20° C., zoodat het in de vroegere proef op toeval zou kunnen berusten.

III. De contrôle op 5 Juni vertoonde stadia van III tot IV<sup>+</sup> (en een niet-normalen bol in stadium II<sup>+</sup>).

Bij de niet-gerooide bollen waarvan het loof alleen was afgesneden, was nu de uitslag de volgende: Van 19 bollen, waarvan op 23 April het loof was afgesneden, hadden op 31 Juli 4 een bloem gevormd; van de 20-tallen die op 20 Mei en 5 Juni waren behandeld, vertoonde elke groep 19 bloemen, terwijl 1 bol bladvormend was gebleven.

Volgens den toestand op 5 Juni is deze uitkomst normaal; dat een enkele bol geen bloem vormde, kan in gewone gevallen ook wel eens voorkomen.

De bollen van 20 Mei, die dus niet konden assimileeren, maar in den grond bleven staan, vormen inderdaad meer bloemen (19) dan de droog liggende (14 en 15). Dit kan nog wel aan toeval liggen, doordat in dat 20-tal mogelijk bijna alle bollen stadium II hadden bereikt. Maar er is toch kans, dat inderdaad die toestand met intacte wortels in den vochtigen grond iets minder ongunstig is. Merkwaardig is echter, dat bij de groep van 23 April toch 4 van de 19 een bloem vormden. Konden deze 4 dan

de bloem vormen dóór het behoud van de wortels of doordat in den bodem de vochtigheid misschien gunstiger was dan in de thermostaat (70 %)? Maar dan dringt zich dadelijk de vraag op, waarom slechts een klein deel en niet alle een bloem vormden. De verklaring moet waarschijnlijk gezocht worden in het feit, dat de bladeren aan de basis nog een tijd lang door-groeien; bij enkele bollen kunnen die bladresten nog zoover zijn uitge-groeid, dat de hierin gevormde assimilaten de bloemvorming nog juist mogelijk maakten. In tabel 2 (bij 23 Apr. afgesneden) ziet men, dat deze bloemvorming ook eenigszins achterlijk is.

TABEL 2.  
Stadia op 31 Juli na verschillende behandeling.

Stadium	I	VII-	VII	VII+	VII à VIII	VIII-	VIII	VIII+	VIII++	VIII à IX	IX-	IX
23 Apr. naar 13° C.	20											
23 „ „ 20° C.	20											
23 „ afgesneden	15	1	1			1	1					
20 Mei naar 13° C.	6						8	5	1			
20 „ „ 20° C.	5						3	8	4			
20 „ afgesneden	1					1	18					
5 Juni afgesneden	1						11	7	1			
Contrôle 31 Juli							3	3	5	4	3	1

Deze tabel toont nog aan, dat de contrôle, die normaal geplant bleef en kon assimileeren, toch een weinig verder is met de voltooiing van de bloem (in stad. VIII zijn de vruchtbladen aangelegd, — de verdere over-gangsstadia tot IX betreffen alleen de vorming van de paracorolla).

Samenvattend kunnen wij zeggen: dat de narcis, wanneer de bloem-vorming even is ingeleid (stad. II of II+) in staat is de geheele bloem verder af te maken zonder verdere assimilatie en opname van bodemwater; dat bij vroeg gerooide bollen in stadium I of I à II de bloemvorming niet op gang kan komen; dat deze dus niet mogelijk is, wanneer ze niet reeds is *begonnen*; dat de overige proeven het zeer waarschijnlijk maken, dat dit niet-bloemvormen in die gevallen wordt veroorzaakt, doordat de assimilaten van hetzelfde jaar hiervoor noodig zijn of eenigerlei stof uit de bladen.

In tegenstelling hiermee gedraagt zich de hyacinth van gelijken omvang, die midden in de bladvorming, zelfs in Januari, gerooid en droog neergelegd, in staat is een bloemtros te vormen, m.a.w. het hiervoor benoodigde in den bol zelve ter beschikking heeft. Wel draagt onder zulke omstandigheden de bloemtros minder bloemen.

Wageningen, Februari 1936.

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*Differences in the flower-forming capacity of Narcissus Pseudonarcissus and Hyacinthus orientalis.*

(Summary.)

Narcissi form their flowers in the ground already in May and June (HUISMAN and HARTSEMA, 1933). Experiments on flower-formation, therefore, are much more difficult here than in the case of *Hyacinth* and *Tulip*, where the flower is not formed until after lifting. Of the *Hyacinth*, however, we knew that, in whatever time of the year it may be dug up, it stops the leaf-formation at a high temperature ( $25\frac{1}{2}^{\circ}$  C.) and proceeds to flower-formation (BLAAUW, 1920). The substances in the bulb are sufficient for this. In consequence of this observation now Narcissi of equal circumference (15—17 cm) were dug up on the 2<sup>nd</sup> of May and placed at  $9^{\circ}$ — $13^{\circ}$ — $17^{\circ}$ — $20^{\circ}$ — $23^{\circ}$ — $25\frac{1}{2}^{\circ}$  and  $28^{\circ}$  C. with cut off leaves and roots, in order to trace every fortnight by fixations at which temperature the optimum of flower-formation is situated. As a rule the flower-formation has not yet started on the 2<sup>nd</sup> of May; now, however, it appeared from 10 bulbs fixed on that day that a number of bulbs (4 out of these 10) already were in stage II<sup>+</sup>. Only part of the number (about 60 %) still was in stage I or between I and II. Owing to this coincidence the following became apparent:

1. If in the *Narcissus* the flower-formation has not yet begun, it does not start either at any of the temperatures in the lifted bulbs; the growing-point remains in the leaf-forming period (stage I).

2. If, however, the flower-formation is only just started — about the first beginning of spathe-formation (stage II<sup>+</sup>) — the bulb is able readily to perform the whole flower.

Of the c. 40 % of bulbs which thus are able to form the flower the relationship between the temperature and flower-formation could yet be stated. Fig. 2 shows the result, each dot indicating the stage of the bulbs on the successive dates. *In the beginning the optimum of flower-formation*

lies at c. 20° C., gradually shifting to a somewhat lower temperature (c. 17° C.). This optimum corresponds with that of the tulip.

The bulbs which cannot form flower, but continue in that time to split off 1 or 2 leaves, at first (see Table 1) show an optimum at 20 to 23° C., which optimum is finally also shifted to c. 17° C.

With hyacinths the experiment was repeated in 3 groups, in January (A) 12 bulbs being lifted and re-planted in pots, (B) 12 dug up with the roots cut and dried, (C) 12 dug up with the roots as well as the shoots cut off. All 3 groups were placed in the dark at 25½° C. In March, 8 weeks later, it appeared that in all 3 groups the growing-point had ceased forming leaves and had formed a young inflorescence. In group A the average number of flowers per inflorescence was slightly more favourable than in C (see page 408 and 409); in 5 bulbs in A the newly formed growing-point had even started a second small inflorescence. *The hyacinth is indeed able to form flowers without the assimilation of this year and even with cut leaves and roots.* However, the inflorescences are poorer in flowers than when they are normally formed in summer after the time of assimilation.

Renewed experiments with the *Narcissus*, whether it was either laid dry at 13° or 20° C. with the leaves and roots cut off or remained outside in the ground with only the leaves cut off, confirm that *the Narcissus in the leaf-forming period cannot do without the assimilation-period of this year (or any substance from the leaves) for the flower-formation*, but that *if this flower-formation is only just started (stage II+), the flowers are all readily performed*, even though the bulbs lie dry without roots and leaves.

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**Paleontology.** — *On an interseptal Canal-system in the foraminiferal Species Discocyclina papyracea (Bouée).* By M. G. RUTTEN. (Communicated by Prof. L. RUTTEN).

(Communicated at the meeting of February 29, 1936).

The systematic place of the genus *Discocyclina* Gümbel, a genus of Eocene Larger Foraminifera, is a matter of controversy. GALLOWAY (2) places the genus in the family of the *Cycloclypeidae*, which have developed directly from the *Camerinidae*, whereas VAUGHAN (6) places the genus with the *Orbitoididae*, that are placed a long way off from the *Camerinidae* in the system of CUSHMAN (1). One of the main arguments for the systematic place of the genus is the occurrence or the absence of an interseptal canal-system. Such a system is found with the *Camerinidae* and not with the typical genera of the *Orbitoididae*.

SCHENCK (4) described and figured a canal-system in the type species



of the genus, *Discocyclus pratti* (Michelin), giving a full review of the literature on the subject, and by the time of his publication the matter seemed to be definitely settled. In the same year, however, VAUGHAN (5) made canada-balsam preparations of specimens of *Discocyclus perpusilla* Vaughan that were in particularly good state of preservation. He did find the annular and radial stolon-passages, but no trace of a canal-system within the chamber-walls, and consequently concluded that the existence of an interseptal canal-system was not yet proved. The dark lines and granules found in the middle of the chamber-walls of *Discocyclus pratti* — which were described as interseptal canals by SCHENCK — may be also found in specimens of *Lepidocyclus*, and do not, in VAUGHAN's opinion, prove the existence of interseptal canals. Professor VAUGHAN several times urged me to study the question if possible. As he had already made canada-balsam preparations of very well preserved specimens, I did not see any further means of investigating the matter, until I read that GÜMBEL (3) had described the finer structure of the genus *Discocyclus* from iron-impregnated specimens from iron-ore deposits of the Kressenberg in Germany. Professor BROILI of Munich was so kind as to send to the Mineralogisch-Geologisch Instituut at Utrecht specimens collected at the Kressenberg. The specimens of *Discocyclus* (*Discocyclus*) *papyracea* (Boubée) were partly infiltrated with iron ore, and permitted a study of the finer structure, the results of which are published here.

In horizontal section (see figs. 1, 2, Pl. I, fig. 1) are seen the chamber-cavities of the equatorial chambers filled with brown opaque iron ore, connected by large radial and annular stolon-passages. If the section is somewhat oblique, the annular stolons are usually seen close to the upper and lower sides of the chambers, whereas the radial stolons are found at intermediate heights. In both the annular and radial septa are thin brown lines, also formed by iron ore, representing the interseptal canal-system. These fine canals are continuous throughout the annular septa, and from these they enter into the radial septa. The canals of the annular septa are always connected with canals in the radial septa, which lie towards the central part of the fossil. Although the radial septa connect both the outer and inner annular septa of one ring of chambers, the interseptal radial canals never communicate inward with annular interseptal canals. Where the septa are broken by stolon-passages, the canals are seen to connect with these passages.

Owing to the somewhat irregular form of the equatorial layer, we locally find the equatorial chambers cut, and the lateral chambers in other places of the same section. The equatorial chambers communicate with the lateral chambers by irregular stolon passages and by abundant cribri-form perforations through the roofs and floors of the chambers. The lateral chambers communicate with each other (fig. 3, Pl. I, fig. 2) by these same two means, stolons and perforations through roofs and floors. Although the chamber-cavities of the lateral chambers and also the stolon-passages



and the cribriform perforations are entirely filled with iron ore, there is never the least indication of any iron ore filling in the septa between the lateral chambers. As the state of preservation and infiltration is the same as with the equatorial chambers, sectioned at other places of the same fossils, this proves that an interseptal canal-system is only found in the septa between the chambers of the equatorial layer, and is absent in the septa dividing lateral chambers. Neither have I found proof of a canal-system in the roofs and floors of the equatorial or the lateral chambers.

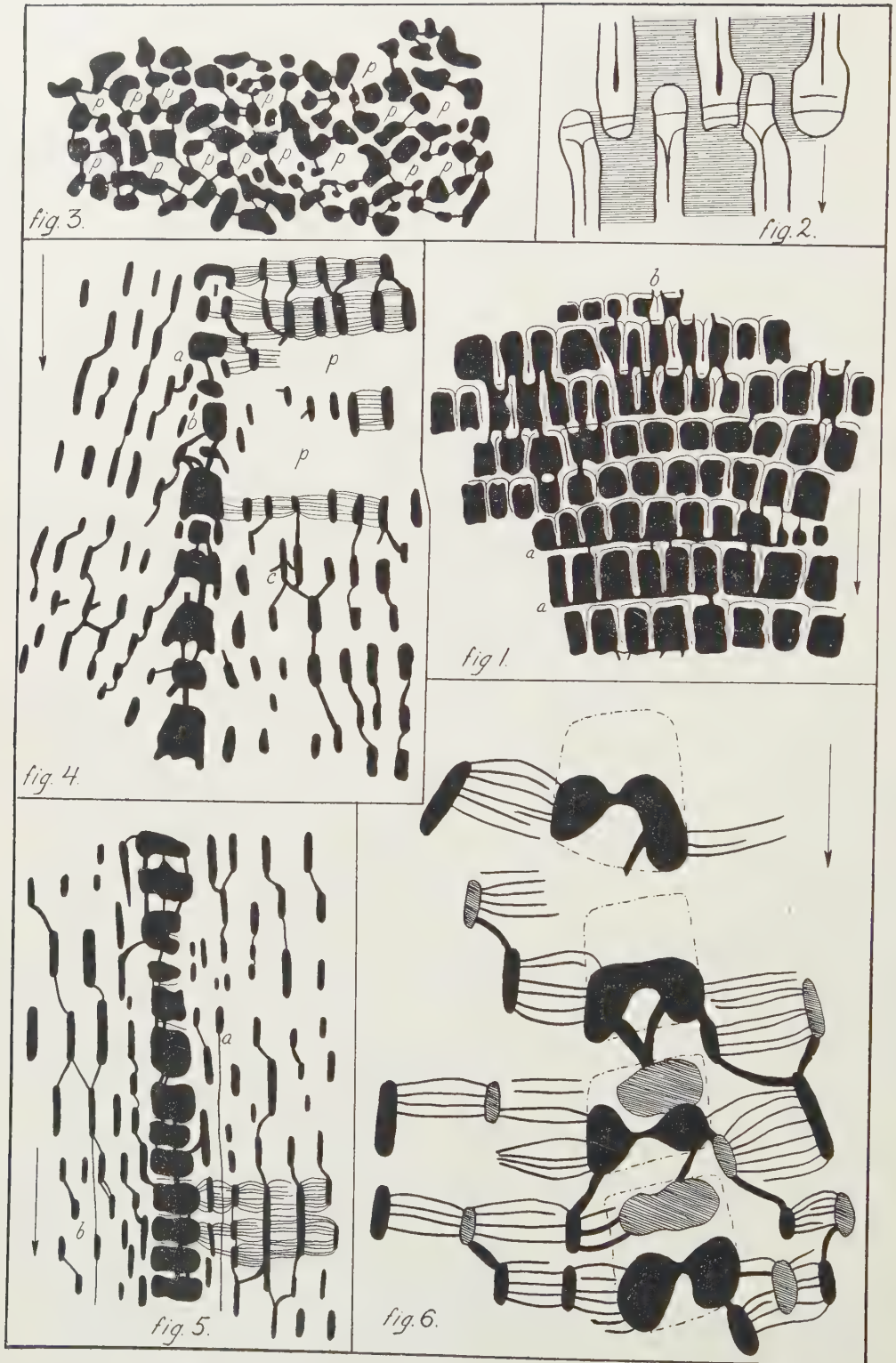
The interseptal canals of the equatorial chambers must have the form of very thin, tabular fissures. Usually these fissures are not wider than  $2\ \mu$  to  $3\ \mu$ . Locally, mostly at the inner end of the radial septa, they widen to a maximum thickness of  $8\ \mu$ . In horizontal direction they are continuous through one annular septal ring and the centrad radial septa. Their height is equal or almost equal to the height of the corresponding septa. For, no matter at which height the equatorial chambers are cut, one always finds the canals exposed within the septa.

In vertical section (figs. 4—6, Pl. I, figs. 3, 4) we see the layer of equatorial chambers, mutually connected by stolon-passages, and the lateral chambers. These are very low, and separated by extremely thick roofs and floors. Equatorial chambers and lateral chambers communicate by stolon-passages and by a great number of cribriform perforations, passing directly through the thick roofs and floors.

Between the equatorial chambers, in the spaces corresponding to the annular septa, we sometimes see the canal-system in these septa, represented by thin, brown lines of iron ore, of about the same height as the cavities of the equatorial chambers (fig. 5, Pl. I, fig. 4). Of the radial septa one usually does not see much. This is due to the fact that the opaque filling of the chamber-cavities shines through the septa, where these are sectioned, and thus they are difficult to distinguish. Only in very thin sections, which are difficult to make, owing to the thin waferlike form of the fossil and its friability, the radial septa are sometimes clearly perceptible (fig. 6, Pl. I, fig. 3).

In textfigure 7 a diagrammatic picture is drawn of the interseptal canal-system in the layer of equatorial chambers, derived from the horizontal and vertical sections of *D. papyracea*.

In the vertical sections a great number of canal-like, iron ore filled, horizontal fissures are found. These are supposed to be layers of lateral chambers, which for the greater part have been suppressed. Locally we see how some of these lines are connected with a lateral chamber, (fig. 5). At the outer end of a vertical section, e. g. in the youngest part of the fossil, a distinct connection between the equatorial chambers and the layers of lateral chambers is found. Every equatorial chamber is the equivalent of one layer of lateral chambers, which are seen to commence at the equatorial chambers. There are, however, a great many more equatorial chambers than layers of lateral chambers. In one specimen



## EXPLANATION OF TEXTFIGURES.

Figs. 1—6. Sections of *Discocyclusa papyracea*. Arrows point to the center of the fossils.

- Fig. 1. Equatorial section.  $\times 80$ . Showing interseptal canal-system, with stolon-passages. Radial passages at *b*, annular passages at *a*.
- Fig. 2. Equatorial section.  $\times 250$ . Showing radial stolon-passages and doubling of the interseptal canals.
- Fig. 3. Horizontal, tangential section, close to the equatorial layer near the outer margin of the fossil Pillars at *p*.
- Fig. 4. Vertical section.  $\times 90$ . Horizontal fissures and the larger part of the cribriform perforations not drawn. Pillars at *p*. Equatorial chambers corresponding each with a layer of lateral chambers near *a* and *b*. Stolon-passages connecting the ends of lateral chambers. Stolons from the middle of a lateral chamber at *c* indicate that this chamber was formed by the melting together of two different lateral chambers.
- Fig. 5. Vertical section.  $\times 80$ . Cribriform perforations and horizontal fissures mostly omitted. Interseptal canal-system in the annular septa between the equatorial chambers. Horizontal fissure widening into a lateral chamber at *a* and *b*.
- Fig. 6. Vertical section.  $\times 250$ . This section passes through four radial septa, which are in alignment. The form of the corresponding chambers is roughly indicated by the dotted line. Part of the chambers are cut near the annular stolons, which therefore seem much larger than they really are. Two chambers of a deeper series partly show through the septa (hatched). The chambers communicate with lateral chambers of the same (black) and of a lower (hatched) level.
- Fig. 7. Diagrammatic section of the layer of equatorial chambers of *Discocyclusa papyracea*, with interseptal canal-system. Stolon-passages are indicated in black. Annular passages are drawn in all annuli, radial passages only in the annuli *a* and *b*. (See page 418.)

I counted about 100 equatorial chambers for half the diameter, corresponding with 25 layers of lateral chambers in the central part of the fossil. The regular conformity, found in the younger parts of the fossil, is obliterated in the more central regions by the wedging out of layers of lateral chambers, passing into these thin horizontal fissures, with only here and there a lateral chamber developed, and by the forming of a great number of pillars. In horizontal, tangential sections the same features are observed. In the central part (Pl. I, fig. 2) the position of the lateral chambers and the pillars is absolutely irregular, but in the outer regions, especially if the section is close to the equatorial layer, the lateral chambers are arranged on regular concentric rings, corresponding with the annuli of equatorial chambers underneath. In fig. 3 this concentric arrangement of the lateral chambers is accentuated by concentric rings of pillars.

Summarizing we can say that the interseptal canal-system of the layer of equatorial chambers, together with the correspondence between the equatorial chambers and the layers of lateral chambers in the younger parts of the fossil, certainly point towards an affinity of the genus *Discocyclusa* with the family of the *Camerinidae* rather than with the *Orbitoididae*.

By dissolving the calcite of an extra-ordinarily fine impregnated

specimen I tried to make an iron ore preparation, analogous to the canada-balsam preparations VAUGHAN made of *Discocyclina perpusilla*. During

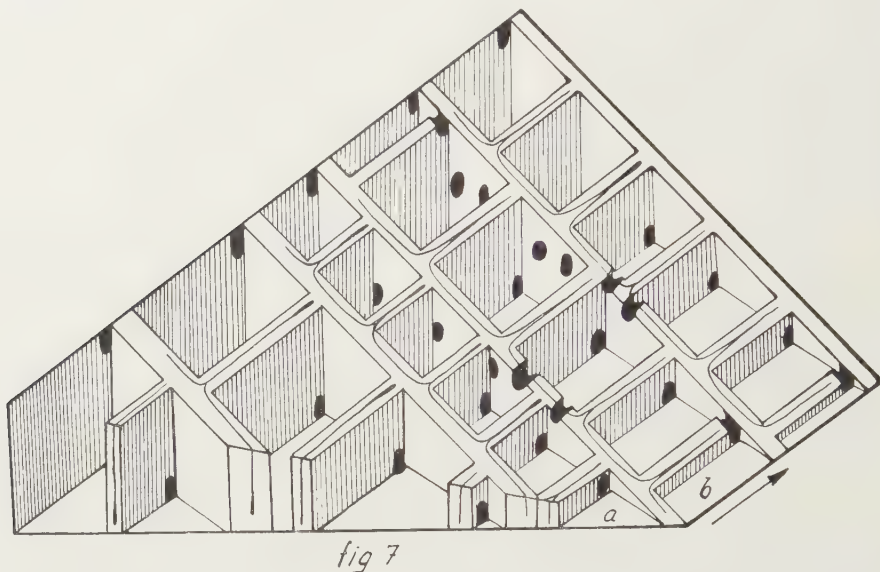


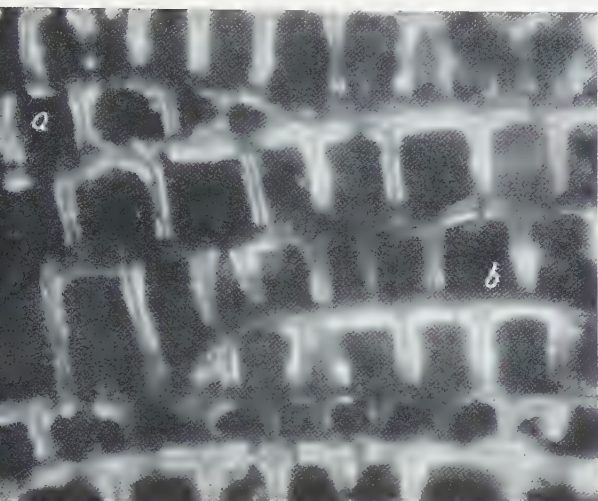
Fig. 7. Diagrammatic section of the layer of equatorial chambers of *Discocyclina papyracea*, with interseptal canal-system. Stolon-passages are indicated in black. Annular passages are drawn in all annuli, radial passages only in the annuli *a* and *b*.

dissolving, however, the thin interseptal canals broke down, being too thin to support themselves. When all calcite was dissolved, the interseptal canals were found only at two places, for the rest being totally destroyed. This explains why VAUGHAN did not find any interseptal canals in *D. perpusilla*. The fissures are so small, that, even if they had been impregnated with balsam, this would break down when the supporting calcite was dissolved and washed away.

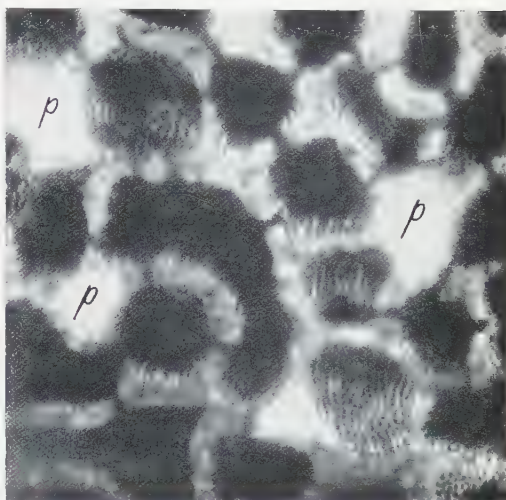
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3. GÜMBEL, C. W.: Beiträge zur Foraminiferenfauna der nordalpinen Eocäugebilde. Abh. Bayr. Akad. d. Wiss., II Cl., Bd. X., II (1868).
4. SCHENCK, H. G.: *Discocyclina* in California. Trans. S. Diego Soc. Nat. Hist., V, 14 (1929).
5. VAUGHAN, T. W.: Descriptions of new species of *Foraminifera* of the genus *Discocyclina* from the Eocene of Mexico. Proc. U.S. Museum, N<sup>o</sup>. 2800 (1929).
6. VAUGHAN, T. W.: Family 47. *Orbitoididae*. In CUSHMAN, J. A.: *Foraminifera*, etc. 2nd Edition (1933).

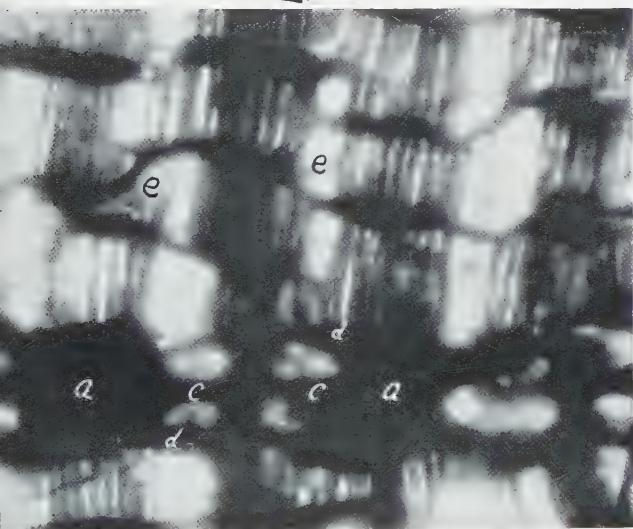




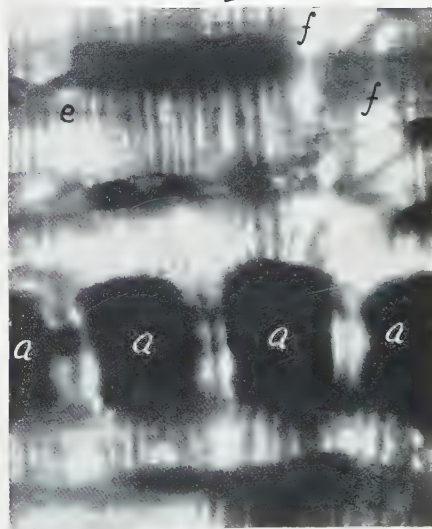
1.



2.



3.



4.

#### EXPLANATION OF PLATE I.

Figs. 1—4. Sections of *Discocyclina papyracea*.

- Fig. 1. Equatorial section.  $\times 170$ . Radial stolon-passages at *a*. Annular passages at *b*. Canal-system in the septa.
- Fig. 2. Horizontal tangential section.  $\times 170$ . Lateral chambers, stolon-passages, cribriform perforations, and pillars at *p*.
- Fig. 3, 4. Vertical sections.  $\times 290$ . Equatorial chambers at *a*. In fig. 3 two chambers are partly concealed by radial septa. Radial stolons at *c*. Annular stolons at *d*. Stolon-passages between lateral chambers at *e*. Horizontal fissures between the lateral chambers at *f*.





**Palaeontology.** — *Smaller Foraminifera from the Marl Zone between Sonde and Modjokerto (Java).* By L. BOOMGAART and J. VROMAN.  
(Communicated by Prof. L. RUTTEN).

(Communicated at the meeting of February 29, 1936).

The present paper is based upon collections, made on the island of Java by the Government Geological Survey, which sent a collection of Mollusca, containing also some smaller Foraminifera, to the Geological Institute at Utrecht.

The Miliolidae and Globigerinidae have been studied by J. VROMAN, who also described the new *Quinqueloculina*; the other families by L. BOOMGAART.

Our thanks are due to Mr. H. E. THALMANN (Palembang), who had the kindness to look over some species, and who gave valuable remarks about them.

The material has been collected in the Marl-zone between Sonde and the meridian a little E. of Modjokerto. The age of the Formations is youngest Tertiary to Quaternary. The succession is as follows:

Kaboehformation	young.
Poetjangan „	
Ngronan „	
Pinggir „	
Soembermiri „	
Klitik „	old.

The results of our determinations are given in Table 2, the findspots are pointed out in Table 1. For the depths we have taken the extreme values given by BRADY (Challenger Report) and CUSHMAN (Lit. 2 and 3). Only the depth of *Spiroloculina costata* HADA has been taken from the publication of Y. HADA (Lit. 7). From the fauna we determined 80 species and varieties. Most of these are recent, except the following:

1. *Quinqueloculina thalmani* VROMAN n. sp.
2. *Lenticulina inornatus* (D'ORB.).  
ALC. D'ORBIGNY: Foraminifères fossiles du bassin Tertiaire de Vienne. Paris 1846, p. 102, Pl. 4, fig. 25 and 26.
3. *Dentalina ?pomuligera* STACHE.  
Novara-Expedition, Geol. I. 2. p. 204, Pl. 22, fig. 31.
4. *Nodosaria fistuca* SCHWAGER.  
Novara-Expedition. Geol. II. p. 217, Pl. V, fig. 36.
5. *Nodosaria ?parexilis* CUSHM. a STEWART.  
Novara-Expedition, Geol. II. p. 223, Pl. V, fig. 52. Lit. 6. p. 55. Pl. 2. fig. 13—15.
6. *Globigerina bulloides* D'ORB., var. *tripartita* KOCH.  
Ecl. geol. Helv., Bd. 19, 3, 1926.

TABLE 1.

	Sheet-numbers of the Topogr. Map of Java (1 : 50 000)	Formation	Sample-Numb. (Geol. Surv. Java)	Localities	Coordinates S. from NW corner of map.	Coordinates E. from NW corner of map.
1	50—XLI B	Riverdeposit.	256	Batang Solo, S E of Sonde	3750	2500
2	" "	Klitikformation	258	Batang Solo	3750	2000
3	51—XLI B	Ngronanformation	14	Kali Djoerit	11250	13500
4	" "	" "	15	Path NW of Klino	11500	14250
5	52—XLI A	" "	29	Kali Kedoengtroetjoek	12100	13250
6	" "	" "	32	S. of Kampong Ngloejoe	14000	16100
7	" "	Kaboehformation	37	Kali Senantok	16750	7000
8	52—XLI B	Soembermiriform.	42	Kali Garoetan	16100	3800
9	" "	" "	43	Kali Garoetan	16150	3950
10	" "	" "	44	Kali Banjoeerip	14250	6900
11	" "	" "	48	Kali Beng	15250	10900
12	" "	Ngronanformation	53	Kali Garoetan	16300	4500
13	" "	" "	57	Kali Bangle	15750	6500
14	53—XLI A	" "	79	Kali Soendo	12750	1100
15	" "	" "	83	Path to Kendajakan	11400	4200
16	" "	" "	102	G. Goewo	4600	14100
17	" "	Poetjanganformation	106	Kali Tjoepak	4250	17250
18	" "	" "	107	Kali Soemberan	5750	18200
19	" "	Pinggirformation	111	Kali Kedoengringin	5100	15400
20	" "	Poetjanganformation	123	Near Kamp. Soemberringin	6000	11600
21	" "	" "	130	Kali Kepoehredjo	6500	17400
22	" "	" "	139	Kali Doeren	6000	14000
23	53—XLI B	Pinggirformation	151	Left-branch Kali Banjoeasin	3600	2900
24	" "	Poetjanganformation	157	Kali Belikdandang	4300	6250
25	" "	" "	158	Banjoebanger	4400	7050
26	" "	" "	165	Kali Gondang	4300	2100
27	" "	" "	170	Kali Belikdandang	4900	6900
28	" "	" "	179	Kali Ngembak	6700	150
29	54—XLI A	" "	216	N. of Kamp. Klagenblandoeng	5400	700

TABLE 2.

[illegible]

7. *Globigerina bulloides* D'ORB., var. *quadripartita* KOCH.  
Ecl. geol. Helv., Bd. 19, 3, 1926.
8. *Globorotalia tumida* (BRADY), var. *flexuosa* KOCH.  
Ecl. geol. Helv., Bd. 18, 2, 1923.
9. *Rotalia beccarii* (L.) var. *atjehensis* V. D. VLERK.

It is remarkable that formations, which contain already such a great number of fossil Mollusca, have such a low percentage of fossil smaller Foraminifera. Total 89 % recent species!

The following species have not been found up to now in fossil state in the Dutch East Indies: *Quinqueloculina bicostata* D'ORB.; *Q. curta* CUSHMAN; *Q. linnaeana* D'ORB.; *Q. aff. pulchella* D'ORB.; *Q. reticulostriata* CUSHMAN; *Q. ?rugosa* D'ORB.; *Q. thalmanni* VROMAN; *Spiroloculina costata* HADA; *Sp. milletti* WIESNER; *Triloculina circularis* (BORNEMANN); *Tr. rupertiana* (BRADY); *Tr. ?terquemiana* (BRADY); *Flintina bradyana* CUSHMAN; *Pyrgo bulloides* D'ORB.; *P. serrata* (BAILEY); *Lenticulina inornatus* (D'ORB.); *L. lucida* (CUSHMAN); *Planularia ?gemmata* (BRADY); *Dentalina ?pomuligera* STACHE; *Nodosaria ?parexilis* CUSHM. a. STEWART; *Guttulina problema* D'ORB.; *G. regina* (BRADY); *Nonion boueanum* (D'ORB.); *Discorbis globularis* (D'ORB.), var. *bradyi* CUSHMAN; *D. vilardeboana* (D'ORB.); *Rotalia beccarii* (L.) var. *atjehensis* V. D. VLERK; *Globigerina inflata* D'ORB.

The living-depth of recent species, as indicated in Table 2, shows clearly that in many cases it is very difficult to use smaller foraminifera as "facies-indicators". This argument is strengthened by the following facts. Without any doubt our fauna is derived from neritical deposits, as is proved by the accompanying mollusks. In general this agrees well with the living-depths of our recent foraminifera, as 67 species or varieties have been found in depths less than 100 fathoms, whilst 5 of these have been collected exclusively in shallow water. On the other hand there are 3 forms which up to now have been found only in deep water, viz.: *Quinqueloculina bicostata* (1584 f.), *Schlumbergerina alveoliniformis* (420 f.) and *Lagena laevis* (254—2435 f.). This indicates that our knowledge of the habitat of these living species is still imperfect and that we must be very prudent, when determining the facies of a deposit from its fauna of smaller foraminifera.

*Quinqueloculina thalmanni* VROMAN, n. sp. (figs. 1—5).

On one side 3, on the other side 4 chambers visible. The individuals are rather strongly compressed; section of chambers oval-oblong, with tendency to triangularity. The chambers are ornamented with a fine network of costae, which is developed best on the outer edge of the youngest chamber. Some individuals (worn off?) show this network to a much smaller extent. The dimensions of the youngest chamber may exceed those of the older ones very strongly. It is somewhat protruding at the base, having there an obtuse point, while its top is provided with a well-developed neck, furrowed longitudinally. These furrows are the



natural continuations of the costae. The aperture is rounded; lip mostly absent. The mouth shows one definite singular claviform tooth. Length up to 1,4 mm; breadth up to 0,9 mm.

This *Quinqueloculina* generally resembles *Q. reticulata* D'ORB. (Challenger Report Pl. IX, fig. 4), but differs from it by: 1. neck provided with parallel furrows; 2. protruding youngest chamber on the lower side; 3. more regular build.

The species has affinities with *Q. kerimbatica* HERON-ALLEN and EARLAND, var. *reticulo-striata* CUSHMAN, 1931, from the Philippine Islands (Lit. 3, p. 347, Pl. 89, fig. 1).

*Rotalia beccarii* (L.), var. *atjehensis* v. D. VLERK. (fig. 6—7).

This species resembles in all respects *Rotalia beccarii* L.; the only difference is the greater number of chambers in the last whorl. For a detailed description we can refer to that of *Rotalia beccarii* L. by CUSHMAN (Lit. 4, part. 8, p. 58—61). Concerning the number of chambers in the last whorl, we calculated the average number of chambers of the last whorl from the specimina, figured by BRADY (Challenger Report) and CUSHMAN (Lit. 2, 3 and 4). The resultant number is 126 chambers in 13 figured specimina, so an average of almost 10 chambers in the last whorl. 22 individuals of the new species gave an average of  $291:22 =$  more than 13 chambers in the last whorl; 12 of the 22 specimens have more than 13 chambers in the last whorl. The greatest number of chambers in the last whorl is 18. Length up to 1,5 mm; breadth up to 0,9 mm. (See: v. D. VLERK, Wet. Meded. Mijnb. Ned. Indië, n<sup>o</sup>. 1, p. 25).



fig 1-5.

Figs. 1—5. *Quinqueloculina thalmanni* VROMAN n. sp.

fig. 6, 7.

Figs. 6—7. *Rotalia beccarii* (L.) var. *atjehensis* v. D. VLERK.

### *Lagenidae.*

It is desirable to give some remarks about the genera *Robulus* MONTFORT, 1801, and *Lenticulina* LAMARCK, 1804. According to CUSHMAN (Lit. 11, p. 177), the only difference between the two genera consists of an enlarged median slit in the middle of the end of the apertural face with the genus *Robulus*. We only used the name *Lenticulina* in consequence of CUSHMAN's suggestion (lit. 11, p. 177). We feel the more justified to do so, because several forms, which by most characteristics agree perfectly, present some species with *Robulina*-like apertures, others with *Lenticulina*-like apertures.

### *Bolivina.*

It is often very difficult to separate the two species *Bolivina hantkeniana* BRADY, and *Bolivina schwageriana* BRADY. In our collection individuals occur "with a keel of varying width and completeness, and short delicate, longitudinal costae", as well as specimens, with "limbate sutures, the limbation taking the form of raised beds or irregular lines of shell-substance on both sides of the test, chiefly near the points of contact of the two opposing series of segments". For figures and a more detailed description of the two species, see BRADY (Challenger Report, p. 424 and 425. Pl. 53, Fig. 16—18 and 24—25).

### *Rotalia indopacifica* THALMANN.

This species is the same as that, figured by CUSHMAN (Lit. 3, Pl. 73) under the name of *Rotalia schroeteriana* P. and J. THALMANN, however, has divided this species into *Rotalia gaimardi* D'ORB. 1826 and *Rotalia conoides* (D'ORB. 1826) (Lit. 14, p. 428—433). The specimina in question do not correspond with them. Mr. THALMANN had the kindness to draw our attention to his new publication (Lit. 15, p. 605), in which he gives a detailed description of specimens of the same species, and calls it *Rotalia indopacifica* n. sp.

*Addendum:* In Table II *Rotalia beccarii* var. *atjehensis* has been erroneously indicated as *Rotalia ijzermanni* n. sp.

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**Biology.** — *Ueber die Frequenzverteilung des Wachstums in homogenem Material.* II. Von C. D. VERRIJP und E. F. DRION. (Communicated by Prof. L. G. M. BAAS BECKING.)

(Communicated at the meeting of January 25, 1936).

### 3. Die Ergebnisse.

Die bei den neun Längemessungen erhaltenen Zahlen sind in Tafel I bis VIII verkürzt zusammengestellt. Das Wachstum der einzelnen Varianten aus den in der ersten vertikalen Spalte angegebenen Klassen (welche sich auf den Anfang der Periode beziehen), ist in den nächsten Spalten dargestellt; die Totalzahlen der horizontalen Reihen, deren Mittelwerte, dividirt durch die Anzahl Tage der betreffenden Periode, und die Streuungen befinden sich in den letzten drei Spalten. Die Totalzahlen sind etwas verschieden, da einzelne Pflanzen wegen Krümmung usw. nicht immer genau zu messen waren.

Die Tabellen zeigen unmittelbar, dass Länge und Wachstum zwar verbunden sind, aber locker, im Sinne einer *Korrelation*. Diese Korrelation ist immer schief, in dem Sinne dass die grösseren Pflanzen schneller wachsen als die kleineren, aber weniger schnell als wenn die Korrelation geradlinig wäre.

Die *z*-Funktionen (KAPTEYN—V. UVEN) der Frequenzverteilungen sind in Fig. 2 gezeichnet. Man sieht sofort, dass *alle Verteilungen brachykurtisch sind*. Die Brachykurtosis wird im Laufe der Entwicklung immer ausgesprochener. Die Reaktionsfunktion einer solchen brachykurtischen Verteilung ist für die niedrigen Werte relativ klein, steigt dann an, und wird für die höheren Werte wieder klein. Wenn nun die Wachstums-

geschwindigkeit, wie die Theorie von KAPTEYN—V. UVEN es will, linear von dieser Reaktionsfunktion abhängt, so müsste man erwarten, dass in

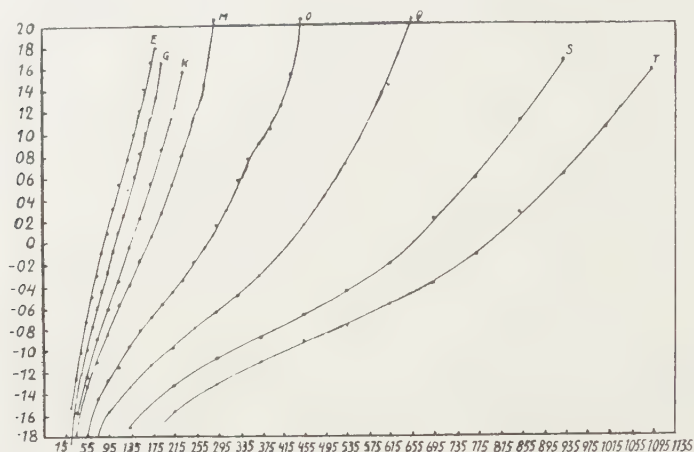


Fig. 2.  $z$ -Funktionen der Längemessungen. Die Achse der Abszissen gibt die Längen in 0.1 mm; Ordinaten:  $z$ -Werte.

unserem Fall, wo die äusseren Umstände für die verschiedenen Varianten möglichst gleich gehalten wurden, die kleinsten und die grössten Pflanzen immer relativ langsam, die mittleren relativ schnell gewachsen wären. Eine solche Verteilung der mittleren Wachstumsgeschwindigkeiten trifft nur für die zweite Periode einigermaßen zu. In allen anderen Fällen nimmt aber, wie schon gesagt, die Wachstumsgeschwindigkeit mit der Grösse nur zu. Die Theorie von KAPTEYN—VAN UVEN kann also zur Erklärung der Wachstumsverhältnisse unserer Pflanzen nicht aufrecht erhalten werden. Dazu kommt, dass man nach dieser Theorie für die relativ schnell wachsenden Pflanzen eine grössere Streuung erwarten müsste als für die langsamer wachsenden. Auch dies trifft, wie die  $\sigma$ -Berechnungen zeigen, nicht zu.

Wie sehr Verschiedenheiten die sich einmal entwickelt haben auch in einem so relativ homogenen Material wie das unsrige, später behalten bleiben, zeigt die Beobachtung einer Gruppierung der Pflanzen nach der Messung der Breite des grössten unteren Blättchen, drei Wochen nachdem die Sprösslinge gepflanzt waren. Diese Messung fand statt am 24. Oktober 1934. Die Verteilung nach den Breiten ergab eine ziemlich regelmässige, ungefähr symmetrische, ausgesprochen brachykurtische Frequenzkurve. Die kleinste gemessene Breite war ungefähr 4.3 mm ( $z = \pm 1.7$ ), die grösste ungefähr 8.5 mm ( $z = \pm 2.1$ ), der Median lag bei  $\pm 6.5$  mm.

Diesen Breiten entsprechend wurde das Material in sechs Gruppen<sup>1)</sup> verteilt. Tafel IX und X zeigen wie sich die Längemessungen dieser Gruppen am 6. Februar und am 5. Juli 1935 zusammensetzten. Die deutliche Korrelationen beweisen das Fortbestehen der schon früh entwickelten Verschiedenheiten der Wachstumsbereitschaft.

<sup>1)</sup> Anfängliche Grenzen der Gruppen: 4.20 mm, 5.40 mm, 6.20 mm, 6.65 mm, 7.10 mm, 7.60 mm, 8.65 mm.

TAFEL I: Wachstum vom 16. November bis zum 11. Januar.

Zunahme der Länge. (mm.)

Masze in mm.	0-1	1-2	2-3	3-4	4-5	5-6	6-7	7-8	8-9	9-10	10-11	11-12	12-13	Total	Mittelwerte per diem in "	σ
0-0.5	—	—	1	—	—	—	—	—	—	—	—	—	—	1	44.6	—
0.5-1.5	3	9	15	22	4	3	—	1	—	—	—	—	—	57	50.5	24
1.5-2.5	—	4	5	32	30	31	18	2	1	—	—	—	—	123	83.7	24
2.5-3.5	—	—	1	20	24	34	35	19	4	1	1	—	—	139	101.6	26
3.5-4.5	—	—	1	3	8	23	31	44	22	4	—	—	—	136	122.0	24
4.5-5.5	—	—	—	—	1	2	13	14	18	10	3	—	1	62	143.2	25
5.5-6.5	—	—	—	—	—	—	3	1	5	4	4	1	—	18	159.6	—
6.5-7.5	—	—	—	—	—	—	—	2	—	1	—	1	—	4	160.7	—
7.5-8.5	—	—	—	—	—	—	—	—	—	1	—	—	—	1	160.7	—
Total . .	3	13	23	77	67	93	100	83	50	21	8	2	1	541		

TAFEL II: Wachstum vom 11. Januar bis zum 6. Februar.

Zunahme der Länge.

Masze in mm.	0-0.5	0.5-1.0	1.0-1.5	1.5-2.0	2.0-2.5	2.5-3.0	3.0-3.5	3.5-4.0	4.0-4.5	4.5-5.0	Total	Mittelwerte per diem in "	σ
0-2	—	2	—	—	—	—	—	—	—	—	2	28.8	—
2-4	9	11	3	3	—	—	—	—	—	—	26	28.8	—
4-6	2	21	24	16	5	1	—	—	—	—	69	49.2	20
6-8	2	13	20	36	28	9	—	1	1	—	110	67.8	26
8-10	1	8	18	29	36	15	8	1	—	—	116	76.8	26
10-12	—	5	9	18	29	29	21	10	3	—	124	96.2	31
12-14	—	1	6	4	13	13	16	6	4	2	65	107.2	35
14-16	—	—	—	—	4	5	5	4	5	1	24	128.2	—
16-18	—	—	—	1	—	5	2	—	—	—	8	105.8	—
18-20	—	—	—	1	—	—	—	—	—	—	1	67.3	—
Total . . . .	14	61	80	108	115	77	52	22	13	3	545		



TAFEL III. Wachstum vom 6. Februar bis zum 11. März.  
Zunahme der Länge.

Masze in mm.	0-0.5	0.5-1.0	1.0-1.5	1.5-2.0	2.0-2.5	2.5-3.0	3.0-3.5	3.5-4.0	4.0-4.5	4.5-5.0	5.0-5.5	5.5-6.0	Total	Mittelwerte per diem in $\mu$	$\sigma$
2-4	3	8	6	—	—	—	—	—	—	—	—	—	17	25.4	—
4-6	1	4	14	17	2	1	—	—	—	—	—	—	39	44.9	—
6-8	—	3	12	21	18	14	1	—	—	—	—	—	69	59.8	13
8-10	—	—	3	13	25	30	11	5	1	—	—	1	88	78.2	21
10-12	—	—	1	3	14	31	25	23	5	1	—	—	103	93.2	19
12-14	—	—	2	2	5	21	34	25	12	3	—	—	104	100.4	21
14-16	—	—	—	—	1	10	12	20	12	5	—	1	61	111.4	20
16-18	—	—	—	—	1	5	9	13	9	4	—	—	41	111.8	19
18-20	—	—	—	—	—	2	2	5	6	3	2	—	20	122.7	—
20-22	—	—	—	—	—	—	—	1	1	—	—	—	2	121.2	—
Total	4	15	38	56	66	114	94	92	46	16	2	2	545		

TAFEL IV. Wachstum vom 11. März bis zum 27. März.  
Zunahme der Länge.

Masze in mm.	0-0.5	0.5-1.0	1.0-1.5	1.5-2.0	2.0-2.5	2.5-3.0	3.0-3.5	3.5-4.0	4.0-4.5	4.5-5.0	5.0-5.5	5.5-6.0	6.0-6.5	Total	Mittelwerte per diem in $\mu$	$\sigma$
2-4	5	1	3	—	—	—	—	—	—	—	—	—	—	9	39.9	—
4-6	3	8	2	1	—	—	—	—	—	—	—	—	—	14	51.3	—
6-8	—	8	12	12	7	1	—	—	—	—	—	—	—	40	94.5	—
8-10	—	5	11	19	10	6	5	—	—	—	—	—	—	56	107.1	44
10-12	—	1	8	14	18	14	7	3	—	—	—	—	—	65	142.6	43
12-14	—	—	1	7	23	23	16	13	3	1	1	—	—	88	179.0	46
14-16	—	—	1	1	7	17	20	23	11	5	—	—	—	85	210.6	45
16-18	—	—	—	—	1	8	13	21	20	14	7	—	—	84	248.1	46
18-20	—	—	—	—	—	2	6	13	15	12	7	1	—	56	264.5	43
20-22	—	—	—	—	1	1	1	5	8	9	2	3	—	30	268.8	—
22-24	—	—	—	—	—	—	2	2	7	4	3	1	—	19	277.1	—
24-26	—	—	—	—	—	—	—	—	—	1	1	—	1	3	338.6	—
Total	8	23	38	54	67	72	70	80	64	46	21	5	1	549		

TAFEL V. Wachstum vom 27. März bis zum 30. April.  
Zunahme der Länge.

Masze in mm.	0—1.5	1.5—3.0	3.0—4.5	4.5—6.0	6.0—7.5	7.5—9.0	9.0—10.5	10.5—12.0	12.0—13.5	13.5—15.0	15.0—16.5	16.5—18.0	18.0—19.5	Total	Mittelwerte per diem in $\mu$	$\sigma$
1—5	1	8	4	—	—	—	—	—	—	—	—	—	—	13	70.5	—
5—9	—	3	18	9	7	1	1	—	—	—	—	—	—	39	140.8	86
9—13	—	1	10	14	23	22	8	5	1	—	—	—	—	84	209.1	64
13—17	—	—	1	—	8	20	42	34	17	4	1	—	—	127	302.1	56
17—21	—	—	—	—	1	8	38	35	23	14	11	1	1	132	342.9	65
21—25	—	—	—	—	—	—	13	21	30	21	5	5	3	98	379.9	64
25—29	—	—	—	—	—	—	1	5	3	10	16	4	—	39	428.2	56
29—33	—	—	—	—	—	—	—	—	—	2	1	—	—	3	433.8	—
Total	1	12	33	23	39	51	103	100	74	51	34	10	4	535		

TAFEL VI. Wachstum vom 30. April bis zum 15. Mai.  
Zunahme der Länge.

Masze in mm.	0—2	2—4	4—6	6—8	8—10	10—12	12—14	14—16	16—18	18—20	20—22	22—24	Total	Mittelwerte per diem in $\mu$	$\sigma$
1—5	1	—	—	—	—	—	—	—	—	—	—	—	1	66.7	—
5—9	2	10	2	—	—	—	—	—	—	—	—	—	14	200.0	—
9—13	1	1	12	8	2	—	1	—	—	—	—	—	25	402.7	—
13—17	—	—	1	10	15	16	4	—	—	—	—	—	46	635	135
17—21	—	1	—	—	6	10	17	9	—	—	—	—	43	811	159
21—25	—	—	—	—	1	10	23	24	13	—	—	—	71	938	131
25—29	—	—	—	—	—	3	18	47	27	1	—	—	96	1004	107
29—33	—	—	—	—	—	3	4	22	30	12	3	1	75	1085	145
33—37	—	—	—	—	—	1	7	18	33	33	2	—	94	1136	135
37—41	—	—	—	—	—	—	—	4	19	14	4	1	42	1200	119
41—45	—	—	—	—	—	—	—	1	7	12	4	1	25	1251	—
45—49	—	—	—	—	—	—	—	—	—	4	—	—	4	1267	—
Total	4	12	15	18	24	43	74	125	129	76	13	3	536		

TAFEL VII: Wachstum vom 15. Mai bis zum 11. Juni.  
Zunahme der Länge.

Masse in mm.	0—4	4—8	8—12	12—16	16—20	20—24	24—28	28—32	32—36	Total	Mittelwerte per diem in $\mu$	$\sigma$
1—9	2	1	—	—	—	—	—	—	—	3	123	—
9—17	2	11	9	—	—	—	—	—	—	22	269	—
17—25	—	1	17	15	8	—	—	—	—	41	442	—
25—33	—	—	—	17	29	5	—	—	—	51	632	92
33—41	—	—	—	4	31	44	19	—	—	98	784	118
41—49	—	—	—	1	18	70	66	7	1	163	869	117
49—57	—	—	—	—	2	21	55	38	4	120	989	127
57—65	—	—	—	—	—	3	17	19	1	40	1030	—
65—73	—	—	—	—	—	—	—	2	—	2	1111	—
Total . .	4	13	26	37	88	143	157	66	6	540		

TAFEL VIII: Wachstum vom 11. Juni bis zum 5. Juli.  
Zunahme der Länge.

Masse in mm.	2—4	4—6	6—8	8—10	10—12	12—14	14—16	16—18	18—20	20—22	22—24	24—26	Total	Mittelwerte per diem in $\mu$	$\sigma$
1—9	1	—	—	—	—	—	—	—	—	—	—	—	1	136	—
9—17	1	3	6	1	—	—	—	—	—	—	—	—	11	285	—
17—25	—	2	2	2	—	1	—	—	—	—	—	—	7	357	—
25—33	—	—	5	10	4	1	2	—	—	—	—	—	22	438	—
33—41	—	—	2	10	7	5	—	—	—	—	—	—	24	466	—
41—49	—	1	—	3	15	10	9	2	—	—	—	—	40	564	110
49—57	—	—	1	3	15	14	9	4	1	1	—	—	48	591	123
57—65	—	—	2	4	6	36	25	14	6	2	—	1	96	652	132
65—73	—	—	1	—	7	33	44	27	10	3	—	—	125	685	107
73—81	—	—	—	1	1	11	40	18	8	4	—	—	83	697	74
81—89	—	—	1	—	1	7	16	28	5	7	—	1	66	752	103
89—97	—	—	—	—	—	1	2	6	5	4	—	—	18	818	—
97—105	—	—	—	—	—	—	—	1	—	—	—	—	1	772	—
Total . . .	2	6	20	34	56	119	147	100	35	21	—	2	542		

TAFEL IX. Verteilung am 6. Februar 1935.  
Gruppierung nach der Messung am 24. Oktober 1934.

LÄNGEMESSUNG.	Masze in mm.	G <sub>1</sub>	G <sub>2</sub>	G <sub>3</sub>	G <sub>4</sub>	G <sub>5</sub>	G <sub>6</sub>	Total
	1.5— 2.5	2	—	—	—	—	—	2
	2.5— 3.5	11	2	—	—	—	—	13
	3.5— 4.5	6	1	1	—	—	—	8
	4.5— 5.5	13	6	2	1	—	—	22
	5.5— 6.5	15	12	1	0	—	—	28
	6.5— 7.5	15	14	4	1	1	—	35
	7.5— 8.5	6	18	9	4	1	—	38
	8.5— 9.5	5	15	15	6	2	—	43
	9.5—10.5	1	23	18	13	2	—	57
	10.5—11.5	—	10	21	14	8	1	54
	11.5—12.5	—	5	12	19	5	4	45
	12.5—13.5	—	0	13	23	15	4	55
	13.5—14.5	—	1	6	12	12	6	37
	14.5—15.5	—	1	4	6	18	9	38
	15.5—16.5	—	—	1	2	9	12	24
	16.5—17.5	—	—	—	1	2	9	12
	17.5—18.5	—	—	—	1	5	7	13
	18.5—19.5	—	—	—	—	1	10	11
	19.5—20.5	—	—	—	—	2	3	5
	Total	74	108	107	103	83	65	540

TAFEL X. Verteilung am 5. Juli 1935.  
Gruppierung nach der Messung am 24. Oktober 1934.

LÄNGEMESSUNG	Masze in mm.	T <sub>1</sub>	T <sub>2</sub>	T <sub>3</sub>	T <sub>4</sub>	T <sub>5</sub>	T <sub>6</sub>	Total
	5.5— 13.5	1	—	—	—	—	—	1
	13.5— 21.5	5	1	—	—	—	—	6
	21.5— 29.5	7	2	—	—	—	—	9
	29.5— 37.5	8	4	1	1	—	—	14
	37.5— 45.5	12	4	3	2	—	—	21
	45.5— 53.3	10	7	1	2	—	—	20
	53.5— 61.5	12	18	6	3	1	—	40
	61.5— 69.5	8	11	12	7	4	—	42
	69.5— 77.5	7	25	19	13	7	5	76
	77.5— 85.5	2	22	30	36	16	10	116
	85.5— 93.5	1	7	24	19	24	11	86
	93.5—101.5	—	4	8	14	19	22	67
	101.5—109.5	—	—	3	4	9	15	31
	109.5—117.5	—	—	1	1	3	2	7
	Total	73	105	108	102	83	65	536

**Comparative Pathology.** — *Hereditary variability in the  $F_3$  seed generation after cross-fertilization of bean races.* By G. P. FRETTS.  
(Communicated by Prof. J. BOEKE).

(Communicated at the meeting of February 29, 1936).

For some years I have been making culture-experiments on beans (*Phaseolus vulgaris*). Two bean races (Line I and Line II), from the laboratory of the late Prof. JOHANSEN, were cross-fertilized and the fertilization products were further cultivated. The measurements, indices and weight were studied. The two lines exhibit fairly large mutual differences. Of the beans of the I line the length is great, the thickness small, the weight large, of those of the II line the length is small, the thickness great and the weight small. Of the I line the indices are low, of the two line they are high.

The hybrid generation ( $F_1$ ) clearly shows matrocliny. This is connected with the fact that of the seed the seed-coat is of maternal origin. The  $F_2$  seed generation possesses a fairly great variation-breadth, the bean yields of the various plants (consequently  $F_1$  plants) do not exhibit any difference. The curves for the examined properties do not offer an indication for the distinction of different types. The averages of the measurements and of the weight are slightly larger than the intermediate values of the averages of the measurements and of the weight of the I and II lines.

The  $F_3$  seed generation has been cultivated in 1934 and is now being studied.

Different beans from the  $F_2$  seed generation have been taken for this purpose; specimens resembling the I type, those resembling the II type, and intermediate forms. As a rule it is not possible to distinguish the types.

According to the following method I have tried to get acquainted with the composition of the  $F_3$  seed generation. The averages for the various properties of the number of examined beans from the cultivated plants display fairly large mutual differences.

I have represented these averages of the examined beans of each plant in the following way by a curve. I have taken as starting-points the intermediate of the harvest 1934 of the I and II lines, and set out these averages by the side of each other on a horizontal line of chequered paper; upwards and downwards the larger and smaller values follow successively (fig. 1). A similar leaf of chequered paper is laid by the side of the scale of fig. 1 in such a way that the average length of the measured bean yield of a plant may be marked in any given place (for the first curve to be made as high as possible) of the vertical length line (L fig. 2).



Then I look up the average breadth of the examined bean yield of this

L B D Gew LB LD BD

165							
4							
3							
2							
1							
160							
159	115						
8	4						
7	3						
6	2						
155	1						
4	110						
3	9	75					
2	8	4					
1	7	3					
150	6	2					
149	105	1					
8	4	70					
7	3	69					
6	2	8	68				
145	1	80	7	7			
4	100	79	6	6	90		
3	9	8	65	80	65	89	
2	8	7	4	79	4	8	
1	7	6	3	8	3	7	
140	6	75	2	7	2	6	
139	95	4	1	6	1	85	
8	4	3	60	75	60	4	
7	3	2	59	4	59	3	
6	2	1	8	3	8	2	
135	1	70	7	2	7	1	
4	90	69	6	1	6	80	
3	9	8	55	70	55	79	
2	8	7	4	69	4	8	
<u>131</u>	<u>87</u>	<u>66</u>	<u>53</u>	<u>68</u>	<u>53</u>	<u>77</u>	
<u>130</u>	<u>6</u>	<u>65</u>	<u>2</u>	<u>7</u>	<u>2</u>	<u>6</u>	
129	85	4	1	66	1	75	
8	4	3	50	65	50	4	
7	3	2	49	4	49	3	
6	2	1	8	3	8	2	
125	1	60	7	2	7	1	
4	80	59	6	1	46	70	
3	79	8	45	60	45	69	
2	8	7	4	59	4	8	
1	7	6	3	8	3	7	
120	6	55	2	7	2	6	
119	75	4	1	6	1	65	
8	4	3	40	55	40	4	
7	3	2	39	4	39	3	
6	2	1	8	53	8	2	
115	1	50	7	2	7	1	
4	70	49	6	1	6	60	
3	69	8	35	50	35	59	
2	8	7	4	49	4	8	
1	7	6	3	8	3	7	
110	66	45	32	47	32	56	

Fig. 1. The underlined numbers, 131, 87, etc. successively represent  $\frac{1}{2}(L_I + L_{II})$ ,  $\frac{1}{2}(B_I + B_{II})$ ,  $\frac{1}{2}(D_I + D_{II})$ ,  $\frac{1}{2}(W_I + W_{II})$ ,  $\frac{1}{2}(LB_I + LB_{II})$ ,  $\frac{1}{2}(LD_I + LD_{II})$ , and  $\frac{1}{2}(BD_I + BD_{II})$  of measured bean yields of the pure lines I and II of the harvest 1934. In each column upwards and downwards the larger and smaller values respectively follow. The measurements in 0.1 mm; the weight in cG. D = Thickness.

plant in the vertical B line of fig. 1, follow the horizontal line through this point until it is intersected by the vertical B line of fig. 2, and here mark the average breadth. In the same way I deal with the average thickness, the average weight and the average indices LB, LD and BD. By connection of the marked points the curve is formed for the averages of the measured bean yield of each plant (figs 2—5).

Fig. 2 represents some curves of measured bean yields of the I line. We see from this that, compared with the intermediate "normal values", the length is great, the breadth smaller and the thickness still smaller. The weight is larger, the indices are smaller. The curves show a striking resemblance. The 3 measurements have a highly corresponding proportion for the different plants. The weight is slightly more divergent. The lines for the 3 indices likewise show a great resemblance as to position and course.

Fig. 3 represents some curves for the averages of the measured bean yield from plants of the II line of 1934. Here also we observe the strong resemblance of the curves mutually and the difference with those of the I line. The length, compared with the intermediate normal values, is small here, the breadth greater and the thickness is greatest of all. The weight is small and the 3 indices are large. The curves for the II line are still more regular than those for the I line.

Fig. 4 represents some curves of the  $F_2$  seed generation, consequently for the averages of the measured bean yield of some  $F_1$  plants of 1934. Fig. 4a contains curves of the  $F_2$  generation, derived from an  $F_1$  generation

L B D Gew. LB LD BD



L B D Gew. LB LD BD



L B D Gew. LB LD BD



Fig. 3.

Fig. 2.

Fig. 2. Curves for the averages of the examined properties of beans from some plants of the I line. Harvest 1934 (cf. text). At the beginning, on the left of each curve, the average length (in 0.1 mm) is recorded.

Fig. 3. Similar curves as in fig. 2 for the II line.

after  $I \times II$  crossings, and fig. 4b contains similar curves after  $II \times I$  crossings ( $F_2$  generations after  $I \times II$  crossings resemble those after  $II \times I$

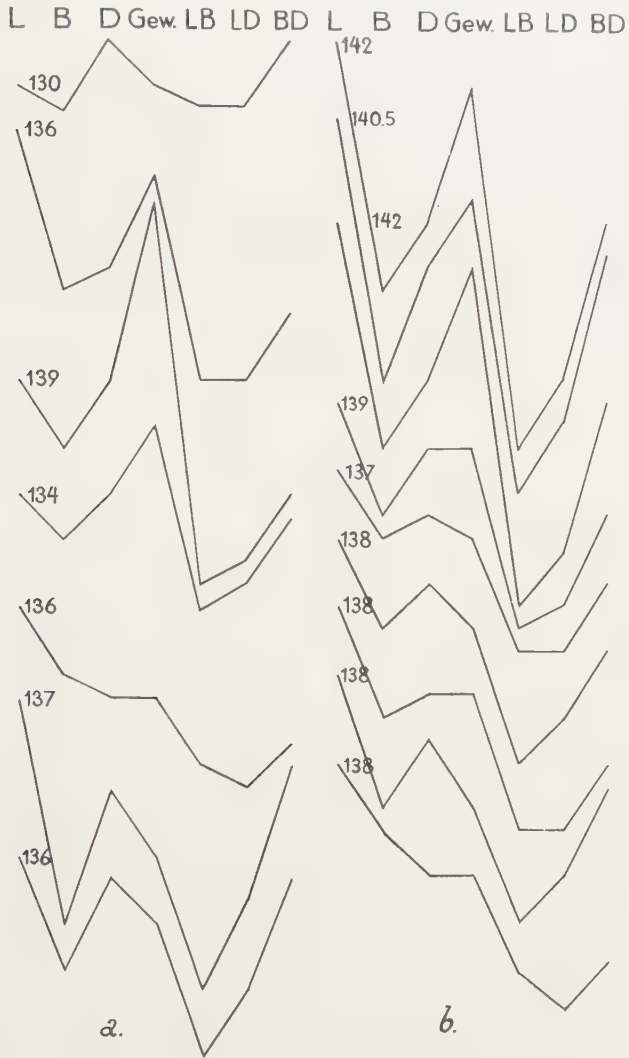


Fig. 4. Curves of bean yields of the  $F_2$  seed generation. a. After  $I \times II$  crossings. b. After  $II \times I$  crossings. Harvest 1934.

crossings<sup>1)</sup>). The curves of fig. 4 show fairly large mutual differences, have a more horizontal course, consequently with regard to the curves of the I and II lines they are intermediate. In all cases the length lies somewhat higher than the breadth, in this respect resembling the curves for the I line (however, there the difference is much larger). In most cases the line connecting breadth and thickness has an ascending course

<sup>1)</sup> G. P. FRETS, *Genetica*, **17**, 54 ff. (1935).

(in 17 cases rising, in 2 cases descending and in one case horizontal), as is the case with the II line (but there more strongly). The line connecting length and thickness nearly always has a descending course (in one case rising, in 2 cases horizontal), as for the I line. The weight more often lies low in the curve (13 times), i.e. as for the II line, than high (7 times), i.e. as for the I line.

The line joining the LB and the LD indices generally rises (13 times), i.e. as for the II line, is sometimes horizontal (4 times) and sometimes descends (3 times), i.e. as for the I line. The line joining the LD and the BD indices always goes up, i.e. as for the I line.

As a rule the indices have a low position on the curves, i.e. as for the I line.

The curves of the  $F_2$  generation consequently have an intermediate course with respect to those of the I and II lines, but correspond slightly more with those of the I line.

For the  $F_3$  seed generation these curves have been made for 128 measured bean yields. In fig. 5 some are reproduced and in table 1 the results have been summarized.

These curves have been placed with regard to each other in descending order of the average length. The curves with the greatest average lengths rather resemble those of the I line, the curves with the smallest average lengths show more resemblance with those for the II line. The method of these curves appears to offer a good possibility to distinguish the hereditary variations.

From table 1 and figs 2—4 we see that, of the curves 1—74 of beans with an average length of 16,5 to 13,6 mM., the line in the curves joining the length and breadth always rises, just as this is always the case with the I line. In the curves 75—128 with an average length of the beans of 13,5 to 11,0 this line nearly always descends (in the last group, 114—128, 14 times in 15 curves), which is always the case with the II line.

The line in the curve connecting the point for the average breadth with that for the average thickness always has, as in the I line, a descending course and in the II line always rises. For the  $F_3$  seed generation this line nearly always descends in the first 15 curves (12 times in 15 curves), consequently as in the I line. In the curves 16—95 this line rises in most of the cases (rises 40 times, descends 30 times) and finally, in the curves 96—128 this line nearly always has a rising course (25 times rising, 3 times horizontal and 5 times descending), as is always the case with the II line.

In the curves 1—50 the point for the average weight lies nearly always high, as is always the case with the I line, in the curves 96—128 it lies nearly always low, as it does always in the II line. In the curves 75—95 the average weight more often lies high than low.

Of the indices the line connecting the LB and LD index always goes down in the I line (once horizontal), always goes up in the II line. For

TABLE 1. F<sub>3</sub> seed generation. Comparison of the averages of the examined properties of the beans for the various plants (cf. text).

Curves	Average length in mm.	L—B			B—D			Weight			Ind. LB—LD			Ind. LD—BD		
		rising	horizont.	descending	rising	horizont.	descending	high	horizont.	low	rising	horizont.	descending	rising	horizont.	descending
1—15	16.5—14.8	—	—	15	2	1	12	15	—	—	5	3	7	15	—	—
16—30	14.7—14.4	—	—	15	9	1	5	12	—	3	8	3	4	13	1	1
31—50	14.3—14.0	—	—	20	9	4	7	18	—	2	9	5	6	20	—	—
51—74	13.9—13.6	—	—	24	12	2	10	16	2	6	9	4	11	22	2	—
75—95	13.5—13.1	5	2	14	10	3	8	11	3	7	8	2	11	19	2	—
96—113	13.0—12.6	11	2	5	14	1	3	1	1	16	15	—	3	14	3	1
114—128	12.5—11.0	14	1	—	14	—	1	—	—	15	11	1	2	4	1	10
I line	15.8	—	—	all	—	—	all	all	—	—	—	1	11	all	—	—
II line	10.6	all	—	—	all	—	—	—	—	all	all	—	—	—	—	all



the  $F_3$  seed generation we find that of the curves 96—128, so of the beans with the small average lengths, this line connecting LB and LD nearly always goes up (26 times up, 5 times down), as is always the case with the II line.

For the curves of plants with a great average bean length the result in this respect is irregular. For the curves 1—15, 51—74 and 75—95 the curve somewhat more often goes down than up (22 times up, 9 times horizontal and 29 times down), as happens always in the I line. In the curves 16—30 and 31—50 the opposite is found (17 times up, 8 times horizontal and 10 times down).

The line connecting the LD and BD indices always rises for the I line and always goes down for the II line. For the beans with the great and less great average lengths, the curves 1—113, this line nearly always goes up (103 times up, 8 times horizontal and twice down), as it always rises for the I line. Only for the group with the smallest average lengths, the curves 114—128, this line goes down in most cases (4 times up, once horizontal, 10 times down), as for the II line.

This investigation of the  $F_3$  seed generation clearly shows that the  $F_3$  generation produces bean yields which represent hereditary variations. The construction of curves according to the method communicated here is very useful for this purpose. The cultivation of a following generation may still more confirm the results.

Thus far the investigation has shown that the cross-fertilization of races with quantitative differences does not lead in following generations to a progeny with intermediate values for the properties of the original forms, but that we can clearly indicate separation. Besides, there is a great environmental influence <sup>1)</sup>

The researches on the  $F_2$  seed generation <sup>2)</sup> thus far did not suggest a means to point out that it contains hereditary variations. Not until the  $F_3$  seed generation had been cultivated, this has been shown. Now that we possess a new method to represent the various examined properties in their relation to each other by the construction of a curve, it is likely that by this method we shall also be able to point out hereditary differences in the individual beans of the  $F_2$  seed generation. This investigation will be made.

A study of the 128 curves of the  $F_3$  seed generation and comparison with those of the I and II lines and the  $F_2$  seed generation is interesting. It appears that the 3 properties, length, breadth and thickness do not mendel completely independently of each other. Of the beans of the I line the length is great and the thickness small, of the beans of the II line on the other hand the length is small and the thickness great. In this

<sup>1)</sup> See e.g. TAVCAR, Variationsstatist. Untersuchungen an reinen Linien. Z.f. ind. Abst. u. Vererb. 1. 1926. E. WARREN, Inheritance in the Foxglove, and the result of selective breeding. Biometrika 14, 103 (1922).

<sup>2)</sup> l.c. p. 61.

large amount of material we do not find bean yields with an average great length and great thickness. For the bean yields with a great average

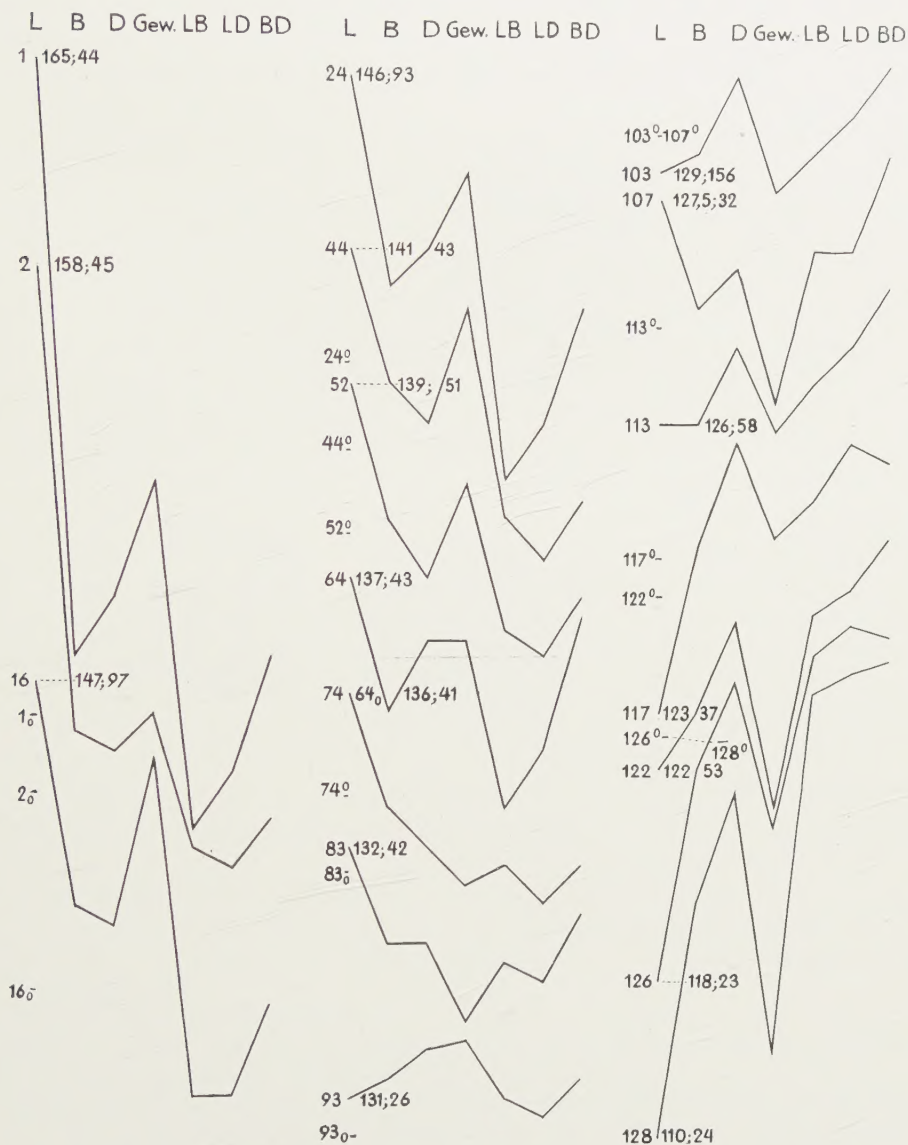


Fig. 5. Curves of bean yields of the  $F_3$  seed generation, Harvest 1934. At the beginning, on the left of each curve, have been indicated by the side of each other: the number of the curve, the average length of the examined bean yield in 0.1 mm and the number of examined beans. On the  $L$  line has also been marked the position of the "normal" length (13.1 mm) for curve (10, 20, etc.).

length, the lines in the curves from  $L$  to  $B$  and from  $B$  to  $D$  go down, as in the I line, and for the beans with a small average length these lines go up, as in the II line. These curves of the two extreme groups are

constructed fairly similarly for each group. The curves of the central group display more mutual differences. This applies also to the indices and the weight. Evidently the properties of the beans of the I and II lines, after cross-fertilization, pass more or less together into following generations. This point also may be investigated more closely by further cultivation.

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